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The Conference on the *Utilization of Chicken Feathers as Filling Materials* was conducted with the assistance and cooperation of the Committee.

THE UTILIZATION OF CHICKEN FEATHERS AS FILLING MATERIALS

A Conference sponsored by the

HEADQUARTERS QUARTERMASTER RESEARCH AND DEVELOPMENT COMMAND U. S. ARMY QUARTERMASTER CORPS

NATICK, MASSACHUSETTS
APRIL 28-29, 1955

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Foreword

The Conference on the modification of chicken feathers was held as part of the broad approach being conducted by the Quartermaster Corps to find a low-cost substitute for waterfowl feathers and down for sleeping bags. Waterfowl feathers and down possess unique properties which make them ideally suited for sleeping bags; however, because of the necessity of obtaining them largely from foreign sources, they are critical materials in times of emergency and, at best, cannot be provided in adequate supply to meet essential military requirements.

The Quartermaster Corps has, for some time, been engaged in a program designed to modify chicken feathers by chemical treatment, so as to improve their properties as a filling material for mixing with waterfowl feathers and down, or as an outright substitute. Sufficient promise has been shown by this approach to indicate that an exchange of information on the research and development activities conducted and sponsored by the Quartermaster Corps in this area should be helpful in expediting the completion of this development.

The scope of the Conference included the presentation and discussion of fundamental studies of the chemical, physical and mechanical properties of feathers and down and applied investigations of chemical modification treatments to improve the bulking value and insulation of feathers.

Participating in the Conference were representatives of government, industry, and universities. Of particular value were the contributions of representatives of the poultry and feather processing industries who would be most intimately concerned with the application of a successful modification treatment for feathers. One of the objectives of the papers presented was to acquaint these industries with the present state of development of the processes and their potential value for producing substitutes and alternates for scarce waterfowl feathers and down.

The papers cover a broad range of interest varying from fundamental studies of the structure of feather keratin, through the development of the acid-alum and glyoxal treatments, to marketing and production information on feathers.

This publication should be of interest to everyone concerned with the production, utilization and technology of feathers and down. It is felt that it will prove to be a valuable reference work to those engaged in the improvement of these materials.

S. J. KENNEDY
Research Director
Textile, Clothing & Footwear Division

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WELCOME TO THE QUARTERMASTER RESEARCH AND DEVELOPMENT CENTER

DR. S. J. KENNEDY:

Ladies and gentlemen, I should like to introduce to you General Calloway, Commanding General of the QMR&D Command.

GENERAL CALLOWAY:

Gentlemen, it is a pleasure and an honor to welcome the Committee on the Development of Substitutes for Waterfowl Feathers and Down to this conference. We in the Quartermaster Corps are well aware of our debt to the country's industrial specialists. Your attendance today is a fine example of this teamwork without which we could not hope to operate successfully. I am concerned with research and development work of the Quartermaster Corps of which this installation is a center, and we acknowledge the contributions of the many experts in highly specialized fields of research. The problem to be discussed today and tomorrow is a good example. In America, we are fortunate that the ties are so cordial between our military and civilians. This is understandable when we stop to think how many Americans have served in uniform, and few in uniform have not engaged in civilian activities. Also, many people of our staff and operating elements throughout the U. S. in particular are themselves civilians.

Your response to our request for information and guidance on the utilization of chicken feathers as filling materials is heartening, and your assistance will advance us toward the solution of this problem. The prime concern of the Quartermaster Corps is to seek new and practical means of providing materials for the combat soldiers of the United States, and we are dedicated to make our combat troops the best equipped of any in the world. Each and everyone today will take satisfaction that you are helping us to fulfill our pledge.

Please accept my sincere thanks and the appreciation of my entire staff for your attendance here at this meeting.

STATEMENT OF THE PROBLEM AND ITS IMPORTANCE TO THE ARMED FORCES

S. J. KENNEDY

Textile, Clothing and Footwear Division,
Quartermaster Research and Development Command

May I express to you first the regrets of Dr. W. George Parks of the National Research Council that he is unable to be present this morning, and in his behalf I should like to cover his part of the program in addition to what I have to say for myself. I should like to take this occasion also to welcome you on behalf of the Textile, Clothing & Footwear Division of this Command, as well as the National Research Council of the National Academy of Sciences under whose auspices this conference is being held. It has been very gratifying to see the wide-spread interest about the work which the QMR&D Command has been conducting in the chemical modification of chicken feathers. Because of the many inquiries received from many sources we felt it would be desirable to hold a general meeting in which the full scope of our work could be presented to those most interested in this field. This plan was formally endorsed by the National Research Council, Committee on the Development of Substitutes for Waterfowl Feathers and Down, of which Dr. Adolf Schubert is the chairman.

Accordingly, plans were made to bring together scientists from universities and government laboratories to present a broad picture of this program and its implications for future research. Similarly, consideration was given to inviting representatives of a broad segment of industry and the educational fields, so they could attend and participate in the discussions to be held. This included agencies of the U. S. Department of Agriculture, which are concerned with poultry feeding and research, poultry processers, feather processers, and related industries. It also included private and government laboratories working on protein research, and all departments of the U. S. and state governments having interest in filling materials.

In order to focus the discussion at such conference upon problems of direct interest to the Quartermaster Corps, it has been the policy to limit attendance to invited guests. However, any person showing an interest in attending has been extended an invitation. Thus, we have representation from a very wide segment of industry concerned with this problem.

Also, may I present the National Research Council Committee; these include: Dr. Schubert, Chairman; Dr. Frederick of the Mellon Institute; Dr. Frishman; Dr. Hegman; Mr. Jespersen; Mr. Ludin; Dr. Krimm; Dr. Lollar, University of Cincinnati; Dr. Stein, of the Medical School of New York City.

Let me extend not only our welcome but also our thanks for your leaving other important duties to be with us today.

I believe the most important point I should make is to invite your attention to some differences between military research and the general field of civilian research. The first point is that we start in our research from the end item and work backward to the raw material. We have very specific objectives in mind and we know what we want in terms of performance. We accordingly try to find materials and construction principles to meet these requirements. This is in contrast to a great deal of research done in civilian laboratories, which is not specifically concerned with ultimate application.

In the second place, we have an urgent need, so we try to see the results of our research as quickly as possible. Our end item today is sleeping bags; we need them today, not a few years from now.

Third, we are a public service enterprise. We are concerned with the saving of human life. Our objective is to preserve the efficiency of the combat soldier to reduce the strain upon his energies. In that way, we have a present opportunity of doing something constructive in every sense of the word.

Fourth, we must not only do a job, but a complete job. We are concerned with the problem from its inception down through application, the development of the end item, and finally turning over the item to procurement. Beyond that, we are concerned with evaluating what we have done. In that respect, we see the research field as a whole, more than most research workers.

Hence, as we present this program to you today, we are looking at it from the standpoint of what the combat soldier is going to have for field sleeping; how to protect him in conditions of extreme cold; the maintenance problem; the laundry problem; the field logistics problem of keeping the bag up with the man, and whether the man can carry the item actually in combat or not.

Suppose we start with our basic problem. Here we have a soldier with our combat load as we visualize it today. The soldier's equipment which he must carry with him includes first of all a rifle; the rifle weighs nine and a half pounds. There is a new one under development probably weighing somewhat less. With the rifle, he has between twelve and thirteen pounds of ammunition. Consequently, he is well loaded before he starts. He will have a sleeping bag which also weighs about nine pounds. The bag itself is six and a half, and the outer case is about two and a quarter pounds. That is a lot of weight. (Demonstration.) This is the present concept of carrying the sleeping bag. As you will see, that is quite compact. It is technically possible for the man to carry it, but there is more weight involved than we would like to see in it. It does have the possibility of being opened out into a very effective piece of sleeping equipment. By fluffing the feathers and down, they achieve thickness, and by thickness and bulk, these trap dead air spaces which, in turn, make it possible to insulate the man against the cold.

We recognize that a piece of equipment of this sort would not always be actually carried by many men into combat, but the important point

which causes us to look to this item of equipment as something which the man can carry under any conditions is the fact he cannot depend upon auxiliary means of transport. Under conditions of extreme cold, actual survival will depend upon his having sleeping gear.

Let me say a word now about the bag as an item of military equipment. If we omit the Revolutionary War and the sufferings at Valley Forge, it will become apparent that most of our military efforts have been in climates where a blanket or two was enough. In the "War Between the States," action was largely in the south. In the Spanish-American War, it was tropical, also, the Philippine Insurrection and the war of the Mexican border. During World War I, the static type of fighting made it possible to get along with blankets. So, it is not surprising that at the outbreak of World War II a field officer made the comment that all a man needs for field equipment was a blanket and a can of beans. It's not hard to understand how that type of thinking would develop. However, before World War II, troops in Alaska recognized that for fighting in extreme cold we had to have something giving far more protection than the blanket. It was recognized we would have to protect men under extreme cold temperatures, as far as forty below zero, and that would also be true for troops in mountainous areas.

Because of greater dependence upon man's own portability as a means of supply, and these rather limited uses of arctic troops and mountain troops, it was possible to provide sleeping bags filled with waterfowl feathers and down—sixty percent down and forty percent waterfowl feathers, in order to make efficient use of the filling material, the waterfowl feathers and down. During World War II, however, it was not possible to provide bags of this type for the entire Army. I believe it was not recognized that a piece of equipment of this sort was needed.

During the Battle of the Bulge, we ran into severe climatic conditions and our troops suffered materially and their fighting condition was seriously lowered. By the end of the war, it had been recognized by the Army that the sleeping bag was a necessary piece of equipment for every combat soldier. Accordingly, provisions were made to acquire sleeping bags as an item of issue for a very large part of our forces. During the Korean situation, this bag filled a tremendous need, and I think it is not too much to say our bag, sleeping, mountain, which was originally developed for mountain troops, was regarded by the combat soldier as the most valuable piece of equipment he had. Furthermore, it is not too much to say that today the combat soldier considers he has a right to expect adequate sleeping gear such as the sleeping bag.

However, we who have worked with this problem and the people in CONARC (Continental Army Command) who have studied the problem recognize that our sleeping bag today is seriously in need of improvement, and a rather broad program is underway to improve it. From the standpoint of design, however, the problem of bulk and

weight still confronts us. Sleeping gear, of this type at least, seems to have a basic contradiction in military requirements. On one hand we want the bulk for dead air spaces for insulation, and on the other hand we want to eliminate that bulk when the man is carrying it. This contradiction can be resolved by stating that a satisfactory sleeping bag material should roll up to a minimum bulk, but have high bulking value when unrolled. Because of this, waterfowl feathers and down has stood out as the material for this purpose. Many materials which have been considered have not equalled it in this respect.

It is our hope in this symposium to establish, from the information coming out in the presentations and discussions, all that can be known at this time with respect to the possibility of using this other material, chicken feathers, as a substitute for waterfowl feathers and down. Here we have a material which is largely an industrial waste material, but which has the capability of being converted into something that will do as good a job as waterfowl feathers and down, or, perhaps, something which will go a long way toward accomplishing this. Perhaps, to make this transformation of this waste material will be a difficult task, but the difficulty itself, it seems to us, may be a simpler task than some alternate suggestions, such as making people in the United States duck eaters rather than people who like fried chicken.

We are all aware of the possibility of developing a synthetic material. We have conducted many studies on a number of them. Some of them have possibilities, but, from a cost standpoint—the cost to the American public, instead of that of utilizing a present waste material—the chicken feather continues to appear very promising to us. It looks like a material which has the capability of meeting our needs. We hope that with the interest which this meeting will stimulate, we will see further progress toward the meeting of this objective.

May I say that the program as planned for today, is for reports on basic aspects of the problem dealing principally with the fundamentals of chicken feather structure. Tomorrow it will be concerned with the application of various kinds of treatments on chicken feathers which will modify them and introduce them into the field of filling materials. The program has been changed somewhat since the original. However, any changes will be announced as we go along, and during the morning we will have additional copies to pass out to you.

With this presentation on behalf of the Textile, Clothing & Footwear Division of the laboratories here, and also on behalf of the National Research Council, I should now like to turn over the meeting to the Chairman of the morning, Dr. Adolf Schubert.

TECHNICAL SESSION NO. 1

DR. ADOLF SCHUBERT, *presiding*

CHAIRMAN DR. A. SCHUBERT:

I would like to express my appreciation for the welcome extended us by General Calloway as well as the hope that this Conference, which I understand is the first that has ever been held on the subject, will reach some of the objectives mentioned by the General.

I also want to thank Dr. Kennedy for giving us such a complete and clear presentation of the problem as well as its importance to the Armed Forces.

This Conference will deal not only with the physical and chemical properties of feathers and down but also with the problem of replacing waterfowl feathers and down by means of chicken feathers which have been chemically and physically treated so as to acquire similar desirable properties.

Before introducing our next speaker I want to reassure some of the Industry Members who are present and have expressed the fear that the papers will be too scientific for them. It is my belief that if this be so, they should receive sufficient mental stimulation so that they will ask questions during the discussion period and we shall do our best to furnish the answers in everyday language. Tomorrow's papers will be devoted to practical problems, processes and statistics.

Our first paper is on the Amino Acid Composition of Feathers and Down by Dr. W. H. Stahl, who is the head of the Analytical Laboratory of the Pioneering Research Division of the QM Command here at Natick; his partner-in authorship is Dr. Walter A. Schroeder who is working with Professors Corey and Pauling, being concerned with the determination of amino acid sequence in proteins, at the California Institute of Technology.

THE AMINO ACID COMPOSITION OF FEATHERS AND DOWN

W. H. STAHL

Head, Analytical Laboratory, Pioneering Research Division, Quartermaster Research and Development Command

DR. W. H. STAHL:

Even casual inspection of a feather reveals a number of parts of obviously different character, and if one studies the literature on the growth and development of a feather one is impressed with the fact that a feather is a highly complex structure. A feather develops from the so-called collar on the papilla at the bottom of the follicle. Experiments have shown that the various parts of the collar and papilla are exceedingly specific in their function of producing individual parts of

a feather. If a transplant of a papilla is made from one part of a bird to another, the feather which develops will be characteristic of the original site from which it was transplanted. Likewise, if a papilla is rotated, the feather will be disoriented. The excision of different parts of the papilla results in feathers with imperfections. It is clear that the various parts of a feather are not merely branchings or extensions of other parts, but originate in altogether different regions of the papilla. Furthermore, the X-ray diffraction pattern of portions of the rachis of a feather is different in appearance from the pattern of material taken from the calamus. I shall define these terms shortly. Data such as these strongly suggest these apparent differences cannot be ignored in investigations designed to determine the structure of so-called "feather keratin." Accordingly, we have felt that it is of importance to prove or disprove whether or not chemical differences, for example in amino acid content, exist in the individual feather parts.

Thus, as part of an investigation of the structure of feather keratin, we have made an exact quantitative determination of the amino acid content of four distinct parts of a feather in order to determine whether or not the composition is uniform. Initially, white turkey feathers have been used for analysis because the absence of color simplified the determinations and because the size of the feathers facilitated their sectioning. Within the last month or so, we have improved upon the techniques and have been able to section much smaller feathers. In addition, analyses have been made of goose feather barbs and of goose down in order to ascertain (1) whether species differences exist and (2) whether various types of feathers from the same kind of bird are identical in composition.

We are also compiling data on the amino acid sequences which are necessary to prove or disprove the structures that have been proposed on the basis of X-ray investigations. Certain configurations require certain minimum side groups in order to allow them to pack in an orderly configuration. It follows that certain amino acids must be present to account for the orderly bending of the chains in assuming their coiled or pleated structures.

Now let us examine a typical feather (Figure 1). The purpose is simply to define the major feather parts that I shall mention throughout the discussion. In this figure, the feather is viewed from the dorsal side, that is, the side which the feather presents to the outside world. The opposite side toward the bird itself is termed the ventral side. The portion of the feather from R to A is above the skin level of the bird and that from C to A is below. The rachis bears the barbs which in themselves are complex structures and support barbules. The barbules of each barb possess hooklets which interlock with the barbules of the adjoining barb. This interlocking of the barbules maintains the general form of the feather. If the hooklets are absent, the feather is fluffy as is often the case near the junction of rachis and

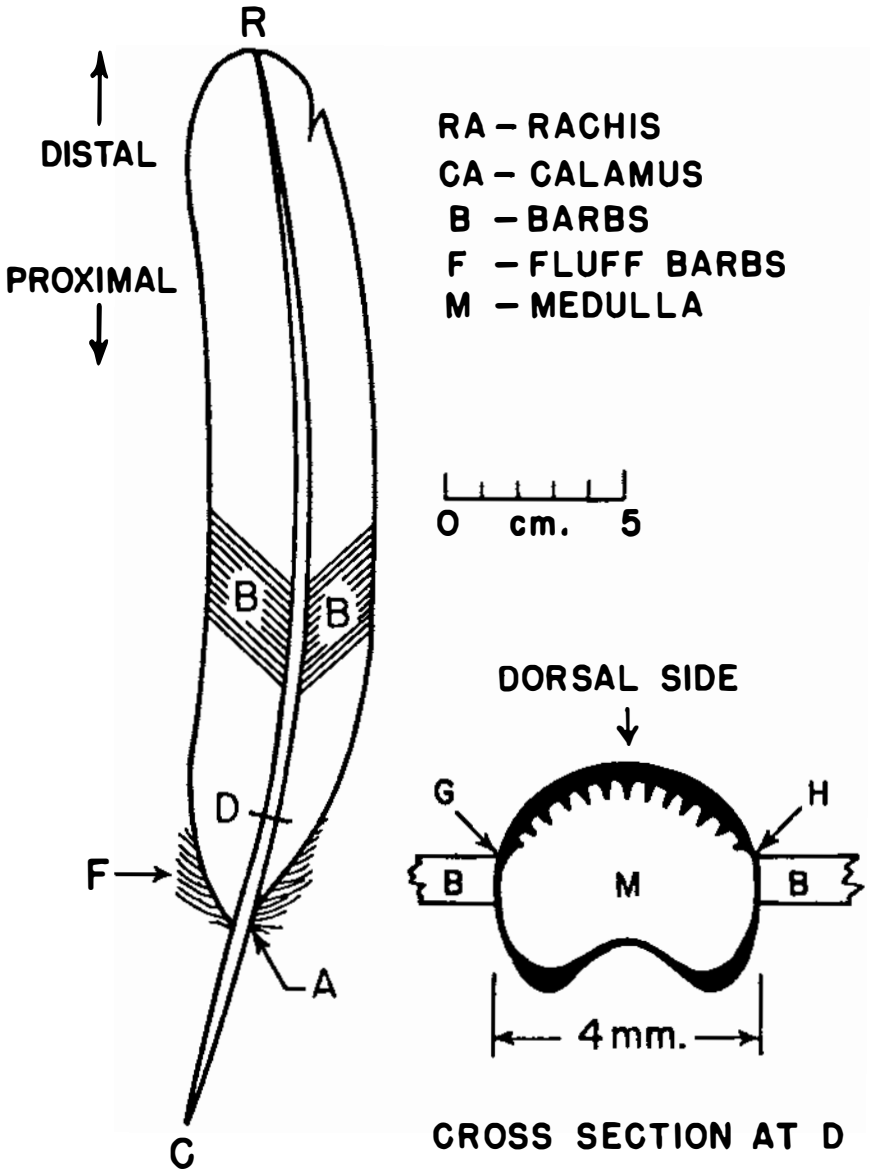

FIGURE 1

Anatomy of white turkey feather: View from dorsal side.

calamus. Throughout its length, the rachis is filled with a pithy cellular substance of low apparent density which is termed the medulla. The barbs also contain medullary material which does not join that of the rachis. The interior dorsal side of the rachis contains grooves which extend from R approximately to A and, like the rest of the interior, these grooves are packed tightly with the medulla. The rachis is thickest on the dorsal side and very thin at the junction with the barbs and at the bottom of the ventral groove. The calamus is the portion below the skin and is essentially cylindrical but slightly thickened on the dorsal side. Thus, the main parts are: rachis, calamus, barbs, fluff barbs, and medulla.

Thus, the four distinct feather parts that have been compared as to amino acid content to note whether or not the composition is uniform are rachis, barbs, calamus and medulla. The feather parts were hydrolized with HCl for periods of 24 and 73 hours and aliquots placed on either starch columns or ion exchange columns and separated by the usual chromatographic technique. It may be interesting to note that only two to three milligram samples are required for this type of analysis. The reason for more than a single hydrolysis time is that certain amino acids are known to be destroyed by hydrolysis. Thus, if one hydrolyzes at two or three lengths of time and extrapolates a curve of concentration versus time to zero time, one will get the true amino acid content of that particular feather. This we have done. Cystine, which does not yield good quantitative results when determined as such, was easily separately determined after its conversion to cysteic acid by oxidation with performic acid. It should be noted that in our hands, we have been attaining an agreement on a single determination in two hydrolysates well within the limits of a plus or minus three to five percent. Accordingly, we suggest the results are accurate to plus or minus two or three percent.

Figure 2 shows a typical chromatogram of a synthetic mixture of acids wherein the quantity of amino acid is plotted on the ordinate and the fraction emerging from the Dowex-50 column is on the abscissa. A specific color is produced in each one of these fractions with ninhydrin and the concentration measured on a spectrophotometer at a particular wave length. The identification of the amino acids in these hydrolysates rests upon the chromatographic behavior of the zones as compared to that of known amino acids. The sequence on a particular type of ion-exchange resin or partition on a starch column is always constant.

In Figure 3 we have a compilation and condensation of results of the quantitative analysis of seventeen amino acids and ammonia in a variety of feathers and feather parts. The most abundant amino acids in feather proteins are serine, glycine, and proline. The first two each constitute about 15% of the residues and the proline about 10%. Alanine, valine, and leucine each compose about 8% of the residues and isoleucine about 4%. Approximately equal residues of aspartic acid and glutamic acid are present and they total about 12%.

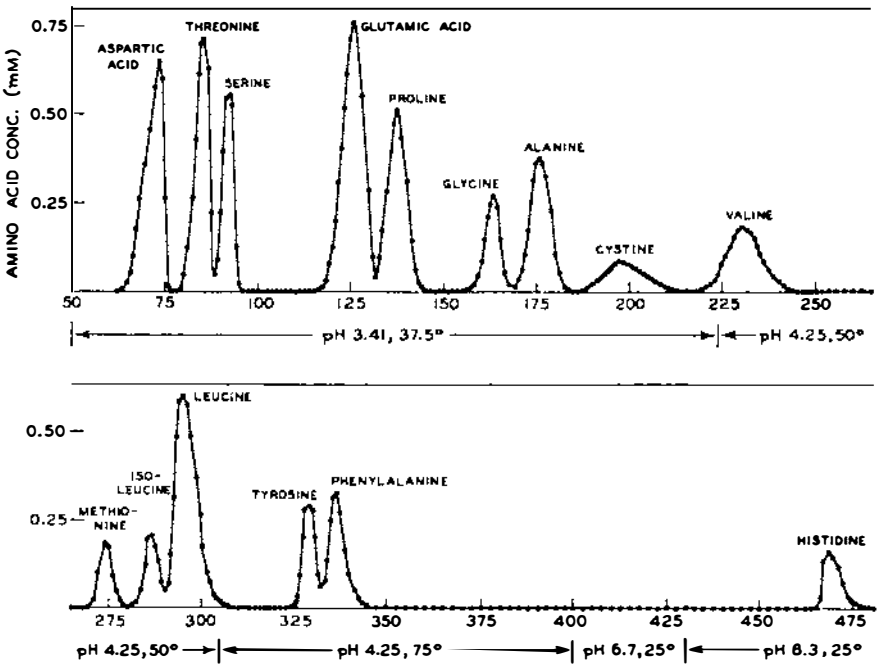

FIGURE 2

Typical chromatogram of a synthetic mixture of amino acids on Dowex-50, as taken from Moore and Stein, J. Biol. Chem. **192**, 664 (1951).

The relatively high ammonia content which is not indicated on this slide would suggest that in the barbs most of the acidic amino acid residues are in the form of glutamine and asparagine while in the other parts only about 75% are in this form. Of the basic amino acids, arginine alone is present in appreciable amount. The residues of basic amino acids total only about half the number of residues of the acidic amino acids.

One of the objectives of the present investigation has been to deter-

	Percent of Residues
Proline	10
Serine + glycine	15
Alanine	8
Valine	8
Leucine	8
Isoleucine	4
Aspartic and glutamic acids	12

FIGURE 3

General composition of feather proteins.

mine whether or not various parts of a feather differ in amino acid composition. Figure 4 brings out a point that we consider should be brought to your attention. Most of our data from the laboratory have been presented in the commonly used system of gram of amino acid per one hundred grams of total feather. If one were to recalculate

	Percent
Barbs	102.0
Medulla	106.6
Calamus	112.6
Rachis	112.0

FIGURE 4

Recovery of total amino acids in white turkey feather parts.

these values on the basis of the loss of a mole of water, as these amino acids exist in a polypeptide chain, then the weight recoveries would all be somewhat under a hundred percent. The ratio, however, is the same. It is apparent that the accounting is more complete in the calamus and rachis than in the barbs and medulla. It is reasonable to conclude that these differences arise largely because of the presence of greater amounts of cell debris in the barbs and medulla; thus, if the various parts are examined microscopically, it is difficult to dis-

Identical	Different
Aspartic acid	Alanine—B[a] < M < C = R
Phenylalanine	Ammonia—B > C = M = R
Proline	Cystine—B > C = M = R
	Glutamic acid—B > C = M = R
Arginine	Glycine—B < C = M = R
Methionine	Isoleucine—B > C = M = R
Serine	Tyrosine—B = R < C = M
Threonine	
Valine	Histidine—B = R ≤ C < M
	Leucine—B < C ≈ M ≈ R
	Lysine—B = M > C = R

[a] B = barbs; C = calamus; M = medulla; R = rachis.

FIGURE 5

Conclusions about the amino acid composition of white turkey feather parts.

cern any cell outlines in the calamus and rachis, but they are very apparent in the medulla, and to some extent also in the barbs which in themselves possess a medulla. Apparently, then, the barbs and medulla contain greater amounts of nonproteinaceous material. Therefore, the following three figures are all based on percentage of total weight of amino acids determined, rather than weight percent of the whole feather.

Examination of the data in white turkey feather parts (Figure 5) shows immediately that each amino acid is present to some extent in each part, that the composition of the parts is very similar, but that

some differences greater than ten percent occur. That is, the differences of plus or minus ten percent of a single amino acid in two comparative feathers or two comparative parts of feathers. On closer study, it is apparent that the calamus and rachis are identical in composition within the limits mentioned above, with the exception of the tyrosine content and possibly the histidine content. Furthermore, the medulla resembles the calamus and rachis very closely, but the barbs are appreciably dissimilar. In noting Figure 5, certain conclusions can be drawn.

For some amino acids, the unhesitating conclusion can be made that the quantities are either identical or that they differ. If they differ by at least ten percent, they are listed above the dotted line. Those amino acids which are listed below the dotted line have been placed in the indicated categories, but their placement is less certain for various reasons. Thus, to interpret in the case of alanine, it is different in the lesser concentration than in the medulla and in the barbs.

Another study with this view of looking for differences of composition within a single feather was done on the sea-gull. Here again, as shown in Figure 6, it is evident that distinct differences exist in the

Serine	$M = C > B$
Glutamic acid	$M = B < C$
Alanine	$B > C > M$
Valine	$C > B = M$

FIGURE 6

Definite differences in amino acid content of parts of sea gull feathers.

morphologically different parts of the feather. We found serine is present in the medulla equivalent to the calamus, but greater than the barb.

A secondary objective of the present work was to determine whether or not there were species variations in feather composition and whether or not there were variations in different types of feather from the same species. One might predict species differences based on the fact that it is already known that, for example, serum albumins from different species differ in number and sequence of amino acids in their peptide chain. In order to ascertain the effects of these variations, goose feather barbs and goose down were chosen for comparison with turkey feather barbs. Barbs and down were selected because of morphological similarities and also because the barbs are easily separated from the remainder of the feather. For those who are not familiar with the construction of a down feather, they might look at Figure 7. One notes the great difference between a down feather in that here you have a truly three-dimensional structure with only a small point of attachment to the body.

Inspection of the data on goose barbs and down (Figure 8) reveals only two possibilities in which the feathers and barbs might differ;

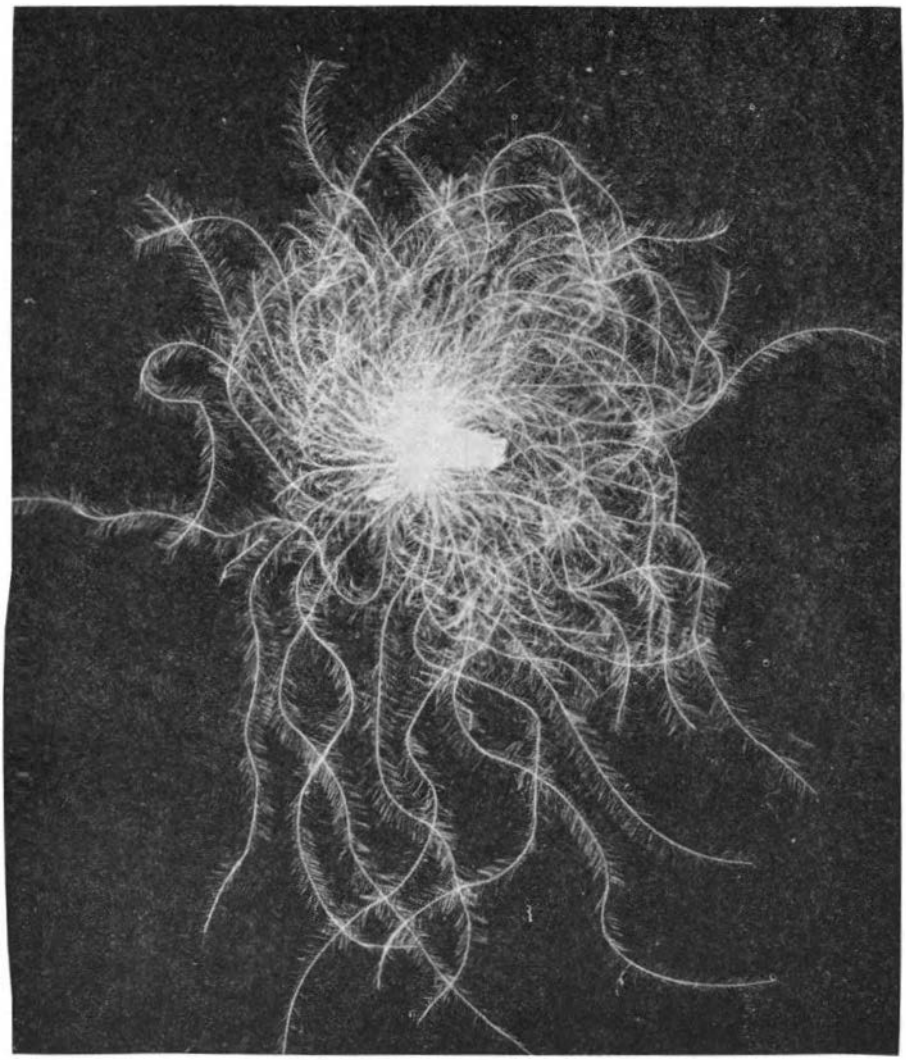

FIGURE 7

Typical goose-down cluster.

Goose barbs Goose down	None

FIGURE 8

Differences between two types of goose feathers.

namely, glycine and tyrosine, and less than two percent. However, both instances are borderline and because duplicate hydrolyses of goose barbs and down were not made, one cannot conclude with confidence that differences exist—probably they do not. Thus, in all likelihood, appreciable dissimilarities in the amino acid content of the two types of goose feathers are negligible.

On the other hand, as shown in Figure 9, it would appear that turkey barbs differ from goose barbs and down in content of cystine, glycine, isoleucine, phenylalanine, proline, tyrosine, and valine. However, the differences in glycine, isoleucine, proline and valine are borderline and probably are not significant. It seems quite definite, however, that turkey feather barbs contain less cystine and tyrosine and more phenylalanine than goose feather barbs or goose down. The sulfur contents substantiate the conclusion about differences in cystine content. As late as yesterday, we completed the cystine analyses on seven differ-

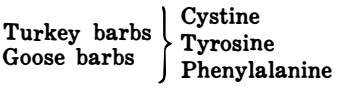

FIGURE 9

Differences between species.

ent species of birds. In the case of the peacock, we get a value of 7.87% as compared to the macaw, which is 9.73%—as much as 19% difference.[1] Thus, we feel a species difference is definitely indicated.

Now, let us turn to another phase of our investigations. The sequence of the atoms of carbon, nitrogen, and oxygen along the backbone of the polypeptide chain is well known. From our crystal structure data we have derived their interatomic distances and bond angles. From their known positions in the chain, we can calculate the contributions of the backbone atoms to the theoretical X-ray patterns for proposed structures and we can then compare these calculated patterns with the experimental X-ray patterns obtained from specific proteins. The calculated patterns are, of course, incomplete, because they do not include the contributions of the side chains. Perfect agreement between the observed and calculated patterns is therefore not to be expected, even if the theoretical structure were exactly right. This discrepancy, and the consequent uncertainty in the interpretation of X-ray patterns, could be removed if we knew (1) the sequence of the amino acid residues in the protein under investigation and (2) the structure, that is, the bond lengths and bond angles, of every residue. The latter information, the structure of each residue, is being obtained from the X-ray crystal analyses of amino acids and simple peptides at the California Institute of Technology, where Dr. Corey is working under a

[1] Since this talk was presented, additional data indicate such widespread differences in cystine in barbs of various species as goose 10.72%, to crane, 4.25%—over 200% difference.

small Quartermaster contract. They are concentrating their work on the simpler protein, gelatin. I can now report briefly on some of our work on amino acid sequences in feather hydrolysates.

If one knows from total analyses that one has a whole group of amino acid residues, we'll say we have this: 25 A, 10 B, and 5 C. The next question that comes up is whether these residues are there as A-B-C, A to A, B to B, or C to C, or any one of the very large number of combinations that these sequences can exist in. Obviously, in attempting to undertake this on a single protein containing twenty-one

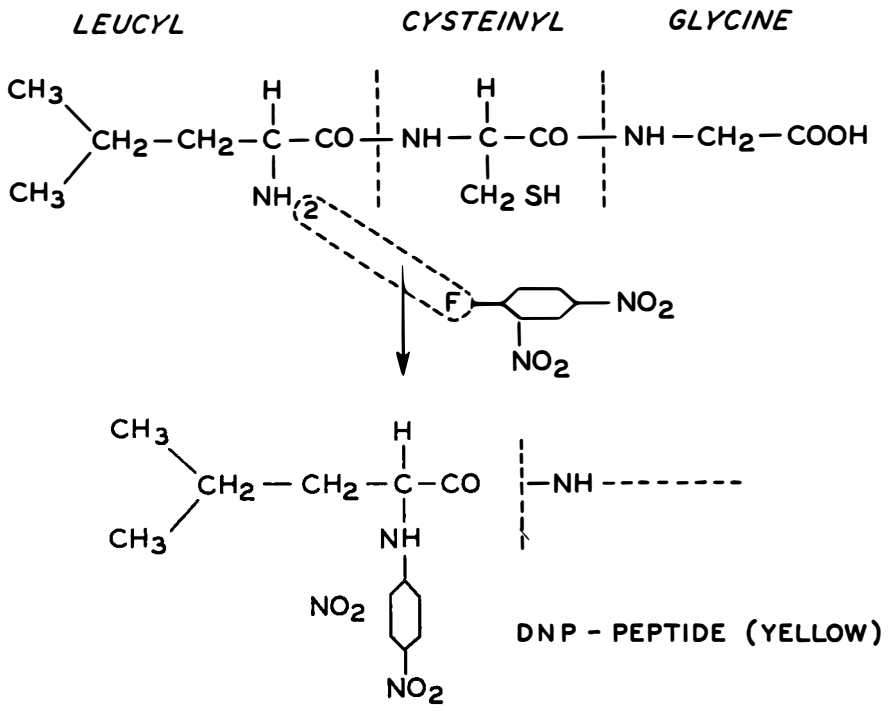

FIGURE 10

amino acids, one cannot find this at one undertaking; so, it is hydrolyzed down to smaller subunits, containing perhaps two, three, or four amino acids. Then one can find the sequence in this small unit.

For the investigation of peptides from partial hydrolysates of feathers, the method of Sanger has been used not only to label the residue at the amino end of a peptide chain, but also for the identification and estimation of the other amino acids of the peptides. The amino acid containing a free N at the end of a chain is often spoken of as the N-terminal amino acid.

According to this method, the dinitrophenol (DNP) peptide obtained by this reaction (Figure 10) is completely hydrolyzed and the N-terminal DNP-amino acid so released is then extracted and identi-

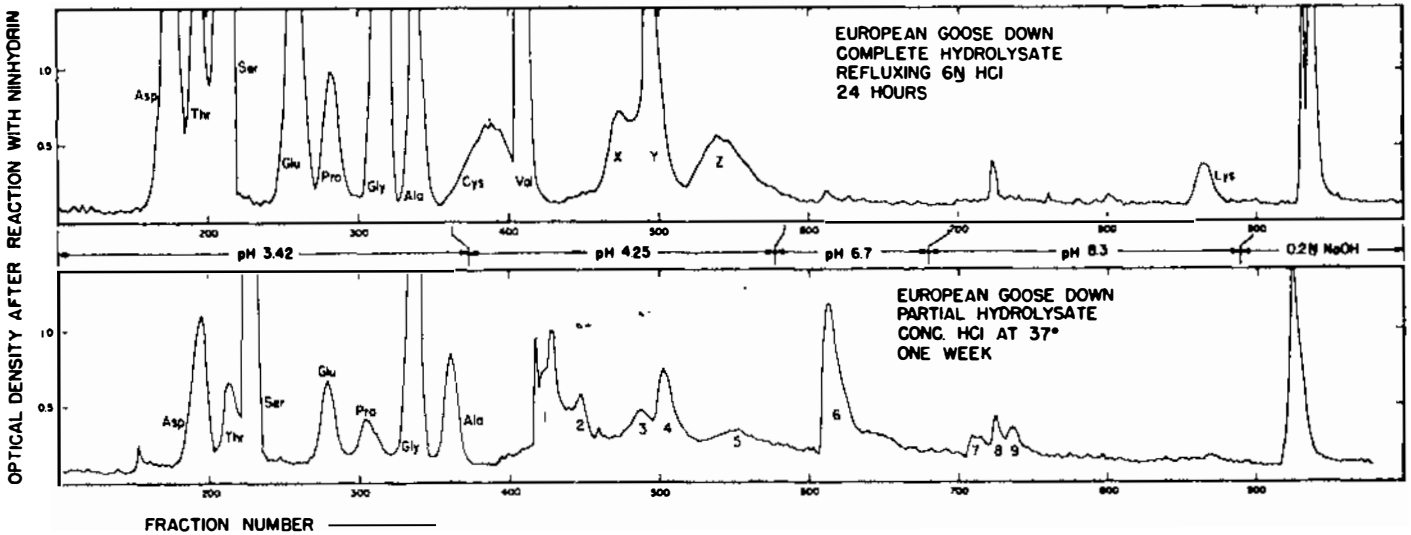

FIGURE 11

Chromatogram of complete and partial hydrolysate of goose down.

fied. In the above tripeptide, the leucyl portion obviously is the N-terminal amino acid in the chain. The remaining amino acids of the peptide which are present as the free amino in the hydrolysate are identified and estimated after conversion to the DNP-amino acids.

Figure 11 compares a complete and partial hydrolysate of European goose down. The top chromatogram is that of a complete hydrolysate, and it may be noted that it is quite well resolved into the individual amino acids. One notes that zones containing peptides in the second chromatogram are ill-formed and in small amount. This is to be expected because goose down also has the normal array of amino acids with none present in exceptional quantity. In the case of the protein gelatin, well-formed peptide zones are obtained since this portion is mainly composed of only four amino acids. Indeed, the case of goose down, and also other feathers, is further complicated by the fact that, in all probability, it is not a single molecular species, whereas a protein such as lysozyme is a homogeneous crystalline protein. We may say with some confidence that zones one, two, and six to nine contain

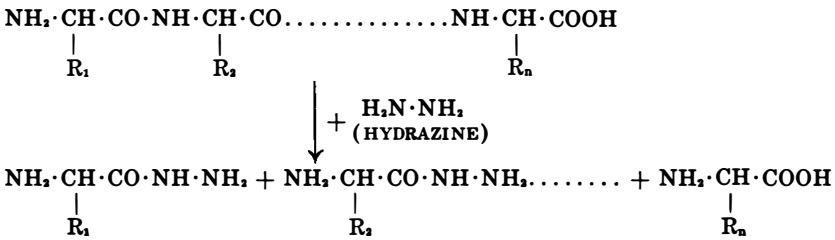

FIGURE 12

peptides, since they are formed in those fractions in which there has been nothing previous to that time. But, zones three to five are probably simply reductions in the amounts of amino acids appearing in the zones marked X, Y and Z.

Large-scale isolation experiments are now underway, and the peptides are in the process of being identified through the formation of the DNP-N-terminal amino acids. A new technique has now been brought to our attention that, should it work satisfactorily, will cut down the length of time on this tedious procedure. If one has a tripeptide or longer peptide, it would simplify things if one could also determine the C-terminal amino acid (see Figure 12). If a protein or peptide is heated with anhydrous hydrazine, the hydrazides are formed of all amino acids except the C-terminal amino acids which are released as the free amino acid. The free amino acid can then be determined by paper chromatography. Or, after dinitrophenylation of the reaction mixture, the C-terminal DNP-amino acid can be separated from the di-DNP-amino acid hydrazides by proper extractive procedures. The C-terminal amino acid in the extract is then identified

and quantitatively estimated. We hope this will cut down the amount of work very demonstrably.

To summarize, the chromatographic analyses have established that differences exist in the amino acid composition of morphologically distinct parts of white turkey feathers. Furthermore, it is probable that different types of feathers from a given species of bird are identical in amino acid composition but that feathers from different species of birds are dissimilar.

The general amino acid composition of the feather proteins is such that about 10% of the residues are proline and another 40% are composed of amino acids with small side chains; that is, glycine, alanine, and serine. Serine and threonine with their polar side chains make up 20% of the residues. If any attempt is to be made to interpret the complex X-ray diffraction pattern of the rachis in terms of the structure of the protein, the general amino acid composition must be kept in mind. For example, it is of interest to note that a proline residue will profoundly influence the configuration of a polypeptide chain and that the feather proteins contain one residue of proline in ten. Therefore, if the proline residues are at all randomly distributed in the feather keratin, it is highly unlikely that the polypeptide chains could assume any of the pleated sheet or simple helical configurations which have thus far been suggested.

CHAIRMAN SCHUBERT:

No doubt a number of you are wondering how or why I, who am in the tanning industry, am concerned with feathers. I was born in the fur industry and my first post-graduate work was with fur. I then graduated into the tanning industry where we have the problem of hair removal as well as hair preservation because by-product hair is one of our sources of income. There is not much difference between fur, hair and finally feathers so that scientific as well as practical experience with fur and hair can be applied with immediate results to feathers.

Some of the members of industry have told me that chicken feathers today are no longer a problem to them. They believe that the production of stock feeds thru hydrolysis and breakdown into digestible amino acids has been the solution. I agree that the demand and production of amino acids for feed purposes is on the increase and new sources are constantly being sought. However, there are a large and constantly increasing number of chickens and industry should have more than one outlet to take care of their feathers. Research as expressed by these papers will provide such outlets.

We are fortunate that for our next speaker we were able to obtain one of the outstanding authorities in the field. Dr. Barbara Low is a Professor and Research Associate at the Harvard Medical School. She is a graduate of Oxford University and obtained her doctorate by majoring in Crystal Chemistry, a subject in which she has continued to specialize, being recognized today as one of the leaders in

this important field. Dr. Low will speak on "Possible Polypeptide Chain Configurations in the Keratin Group of Fibrous Proteins."

POSSIBLE POLYPEPTIDE CHAIN CONFIGURATIONS IN THE KERATIN GROUP OF FIBROUS PROTEINS

BARBARA LOW

Professor and Research Associate,
Harvard Medical School

I would like, before beginning this very general discussion which is really an introduction to Dr. Krimm's more detailed study, to recapitulate some of the chemistry discussed by Dr. Stahl this morning.

When proteins are analyzed they yield α amino acids with the general formula $NH_2CH(R) \cdot COOH$ where R represents one of about twenty-five different possible sidechain groups. Some of these are non-polar, for example, in alanine R is a methyl group. Some are aromatic, in phenylalanine R is a benzyl group. Other amino acid residues are polar, in aspartic acid R is an acetic acid group and in lysine R is an amino butyl group.

In proteins the amino acids are condensed into polypeptide chains with the general formula:

$$NH_2CH(R) \cdot CO \cdot (NH \cdot CH(R)CO)_n \cdot NH \cdot CH(R) \cdot COOH.$$

Not all proteins contain residues of every known amino acid, but the same limited group of amino acids are found in both plant and animal proteins. Once a protein preparation has been purified, its detailed amino acid composition may be determined and if the protein molecular weight is known it may be expressed as moles of amino acid per mole of protein. The α carbon atom of the amino acids is asymmetric except in glycine and there are therefore two isomeric forms of each amino acid. All the amino acids found so far when proteins are analyzed belong to the same L series. Bijvoet and his associates have recently established the absolute configuration of D (+) tartaric acid and thus the corrections on the Fischer convention.

Many proteins contain more than one polypeptide chain. The number of chains may be established by end group analysis. Thus there are known to be four polypeptide chains in insulin and six in horse hemoglobin. In a recent study Sanger and his associates have established in detail the ordered sequences of amino acid residues along the polypeptide chains of insulin. Such detailed and precise knowledge is an outstanding achievement. It represents a tremendous step forward, but it does not present the complete picture of the molecular structure of the protein—insulin.

To illustrate the gaps that it leaves, gaps that physical studies may partially fill, we shall turn to analogy. I have here a knitted glove. In order to describe it so that you may make an identical copy of it, I must first describe the yarn completely, then the knitting pattern, the

design, the color pattern, its size and shape and say also whether it is right handed or left handed. If I unravel it and simply show you the ball of yarn, you will not be able, no matter how accomplished at knitting, to make an identical copy of the original. A ball of yarn is not a glove. In other words, in unravelling the glove I have destroyed or at least lost its special "gloveness"—those qualities which distinguished it from a ball of yarn.

So in insulin, and in all proteins, the special protein nature of the molecule lies deeper than is indicated by a knowledge of the sequences of amino acids along the stretched out chains (the yarn of protein structure).

The phenomenon of protein denaturation appears to be very close to molecular unravelling. Proteins may be treated with certain reagents which break neither the covalent peptide bonds along the chain nor the disulphide $-S-S-$ bonds between chains but which none the less cause profound changes in their properties. In particular denaturation is frequently accompanied by the loss of specific biological properties. It is evident that in the native protein molecule, the polypeptide chains are folded, coiled, or wrapped up in some specific three-dimensional pattern with a place for everything and everything in its place. The specific biological properties of proteins are related to their detailed molecular architecture.

This viewpoint of protein structure was first developed in 1931 by Wu in a most elegant and readable English paper in the Chinese Journal of Physiology. From consideration of the loss of protein-like properties on denaturation, with reagents and under conditions which do not affect amino acids or short-chain peptides, Wu asserted first that proteins must have a highly specific configuration, and second that this must in large part correspond to an ordered "crystalline array."

If the spatial relationships between different parts of the polypeptide chains in a protein molecule are neither random nor fortuitous and more than that if some of the parts appear to be arranged symmetrically with respect to each other in a three-dimensional repeating pattern then two branches of physical optics, X-ray diffraction and infra red spectroscopy, are peculiarly well suited to their study. Of course I am in one sense putting the cart before the horse. The first experimental evidence of symmetrical arrangements within protein molecules came from the X-ray crystallographic studies of protein crystals and protein fibres.

In a crystal the molecules are arranged to form a three-dimensional pattern and this the unit cell, which usually contains only a few molecules, is repeated many times in all three directions. The periodic array of atoms in the crystal may be considered as a periodic distribution of electric density. X-rays are scattered by electrons and the X-ray diffraction pattern depends upon the detailed electron distribution density within the crystal. The geometry of the X-ray diffraction pattern relates to the size and shape of the unit cell. The sym-

metry of the diffraction pattern is related to the symmetry of the inter- and intra-molecular packing. The X-ray intensity distribution depends on the detailed atomic arrangements. Diffraction patterns are not very often observed naturally. If we look at a distant bright light through a fine piece of percale we do see a diffraction pattern which is made up of points and streamers of colored light.

Unfortunately in recording an X-ray diffraction pattern either as a series of spots of varying intensity on a photographic film or by using a geiger counter technique, the phase relationships between the diffracted beams are lost. Complete and detailed structure analyses are possible only if these phase relationships can be established by indirect methods. This has not yet been possible for protein crystals and the X-ray crystallographic studies therefore provided limited and incomplete evidence of protein stereochemistry.

The early X-ray studies of fibrous protein, by Meyer and Mark on silk fibroin, and by Astbury and his co-workers on keratin, showed that in fibrous proteins there are repeating patterns of such small dimensions—that they must arise from order within the molecule rather than from inter-molecular packing. The observations suggest that the polypeptide chains are folded or coiled in some regular array about an axis—the fiber axis—and that neighboring chains are stacked parallel to each other in ordered or partially ordered array. The first chain configurations suggested by Astbury for α keratin were devised to satisfy the three prime requirements of the experimental data. The density of α keratin and indeed of most proteins is about 1.3; the model had to satisfy this requirement. Most configurations proposed seriously do this. The second requirement involves the axial translation of each residue along the fiber axis. It must be adequate to account for the increase in length when α keratin is stretched out to the β form. This cannot be given too precisely as opinion differs concerning the extent of molecular stretching as opposed to inter-molecular slip which is involved. The third requirement comes directly from the diffraction pattern. The diffraction maximum along the fiber axis is at approximately 5 A. The chain configuration must give rise to such a maximum.

Studies have shown that in all probability the polypeptide chains are coiled or folded in globular proteins in similar configurations to those expected for fibrous proteins. We shall henceforth consider the two classes of proteins together.

There is a different approach to this problem of adequate chain configurations which is chemically more satisfying. This rests on the nature of these secondary valence forces which Wu spoke of as holding the molecule together.

Chain folds or coils can be described precisely and in detail only if the unit of chain structure is known precisely and in detail. The dimensions of the peptide chain unit were the starting point for the structures proposed by Pauling and Corey in 1951. They are the fruit of a detailed study of amino acid and peptide structure by Paul-

ing, Corey and Hughes and their associates at the California Institute of Technology over the last fifteen years.

In considering possible configurations they then imposed two further limitations. First that each residue should be completely hydrogen bonded to two of its near neighbors, every residue forming hydrogen bonds in the same way. And second that the hydrogen bond vector should be limited both in length and in direction.

If we consider the first of these limitations it means that all the

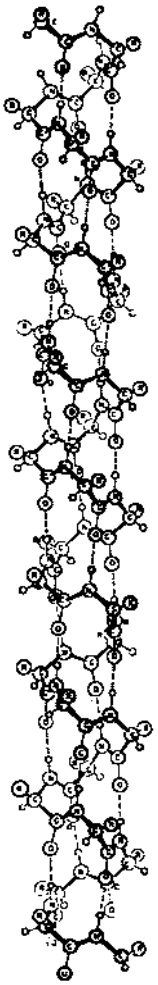

FIGURE 1

A drawing of the α helix. The helix is left-handed. The R and H groups on the α carbon atom should be interchanged in order to correspond to the absolute configuration of the L-amino acid residues in proteins. L. Pauling, R. B. Corey, and H. R. Bronson, Proc. Nat. Acad. Sci., U. S., **37**, 205 (1951).

residues must be equivalent, as all have identical chain environments. That is, they must be coiled up into a helical form.

One helical structure—the α helix—completely satisfies all the chemical criteria for configurational stability. The α helix fits the requirements for an appropriate configuration. The structure is shown in Figure 1. Each succeeding residue $C_1(CO \cdot NH)C_2\cdot$, $C_2(CO \cdot NH)C_3$, etc. lies in one of a zone of vertical planes parallel to the helical axis. The α helix corresponds to the chemical sequence

$$\begin{array}{l} O- - - - - - - - -H \\ \| \qquad\qquad\qquad\qquad | \\ C-(NH \cdot CH(R) \cdot CO)_3 N \end{array}$$

read in either direction with thirteen atoms in the hydrogen bonded loop so formed and with 3.6 residues per unit turn. In the α helix each amide group forms hydrogen bonds with the third amide group beyond it in either direction along the chain.

There are three extended (β) polypeptide chain structures which satisfy the Pauling-Corey chemical criteria. In the fully extended planar polypeptide chain configuration, Figure 2, the predicted repeat

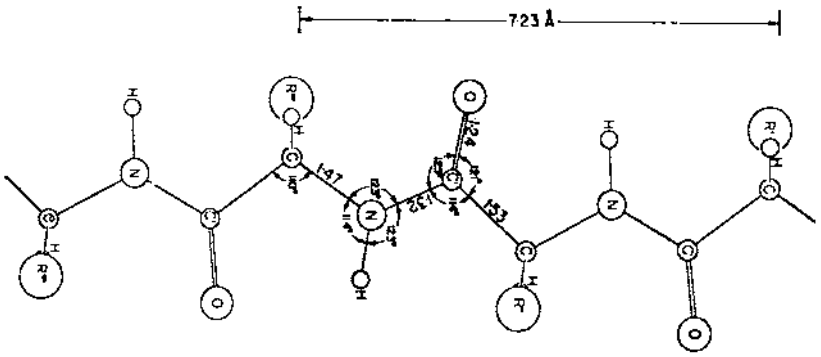

FIGURE 2

Fully extended *trans* polypeptide chain configuration with chain residue bond lengths and bond angles. R. B. Corey and L. Pauling, Proc. Roy. Soc., **B141**, 10 (1953).

distance is 7.23 A. When two such chains are packed side by side to give inter-chain hydrogen bonds there is steric hindrance between opposing side chains unless there are a) both glycyl residues ($-H$) or b) one glycyl and the other alanyl ($-CH_3$) or seryl ($-CH_2OH$). Both the other two structures form lateral inter-chain hydrogen bonds, even if the side chains are bulky. In one arrangement, the parallel pleated sheet structure, Figure 3a, all the chains have the same direction. In the anti-parallel pleated sheet structure, Figure 3b, alternate chains are opposed in direction. The predicted repeat distances along

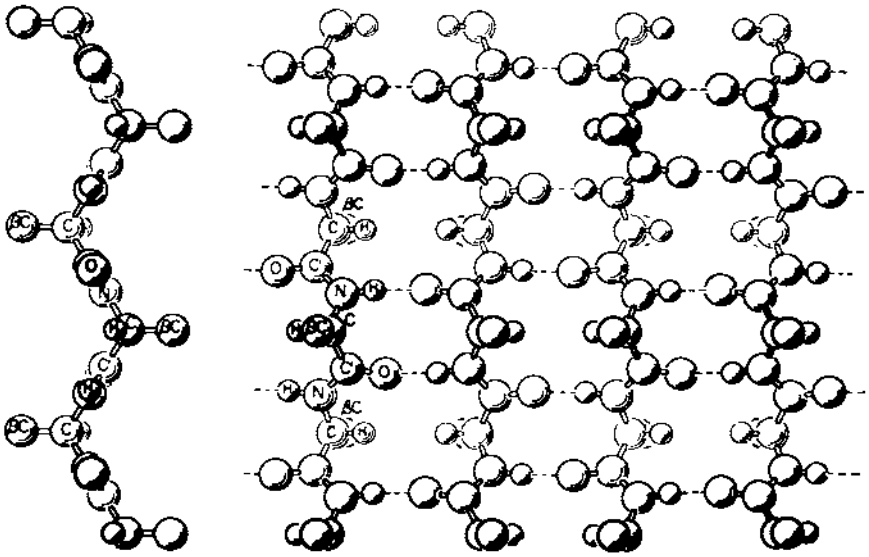

FIGURE 3a

A drawing representing the parallel chain pleated sheet.

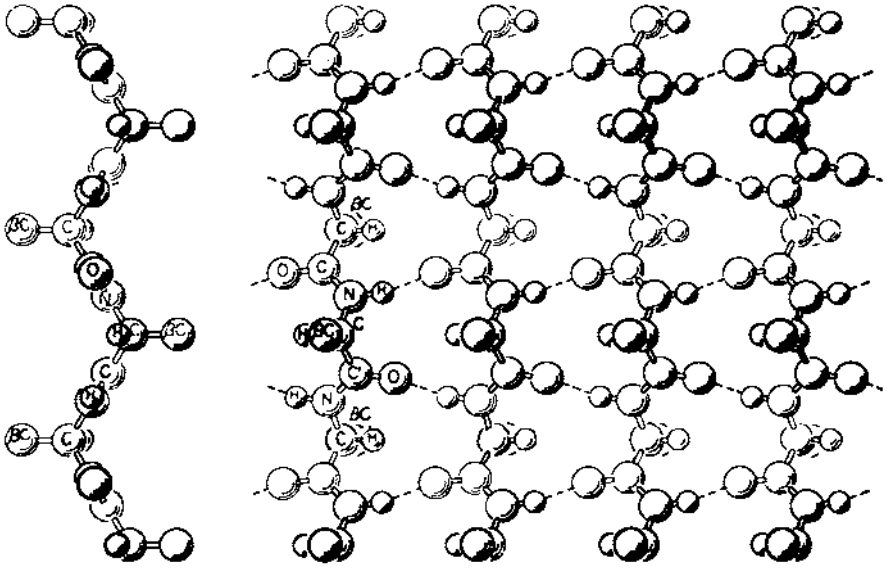

FIGURE 3b

A drawing representing the anti-parallel chain pleated sheet. R. B. Corey and L. Pauling, Proc. Roy. Soc., **B141**, 10 (1953).

the chain direction in both structures are somewhat shorter than the 7.23 A. of the fully-extended structure.

The structure of silk fibroin has been studied in great detail by Marsh, Corey and Pauling; the X-ray patterns obtained were in good agreement with expectation for an anti-parallel chain pleated sheet structure, in which the predominant chain sequence is Gly·X·Gly·X·Gly, where X is alanyl or seryl. The structure may be modified so as to include the larger side chains, such as tyrosyl, in the crystalline component of structure, instead of placing them in amorphous regions as did most earlier investigators who considered this problem.

In the β-keratin structure the parallel pleated sheet arrangement appears the more reasonable model. The hydrogen bonded sheets in both sik fibroin and β-keratin must be held together by interactions between side chain groups, which may be polar or non-polar. The β structure is essentially made up of extended peptide chains in parallel array. The two pleated sheet structures provide nicely for the stereochemical requirements of this mode of packing, and one or other fits the observed X-ray diffraction patterns of most of the β proteins.

In α-keratin the chains are held together by cystine disulphide linkages. The α-β transformation in the k-m-e-f group of fibrous protein is usually considered to take place without $-S-S-$ link breakdown. If the inter-chain cystine linkages are disposed at random the α-β transformation could not take place with the α helix without breaking the disulphide linkages. Indeed simple steric hindrance effects of neighboring side chains would appear to make the transformation extremely difficult, even if the disulphide linkages are located in positions favorable to forming the stretched-out (β) configuration. This difficulty can be avoided by consigning the $-S-S-$ linkages to the non-oriented regions of the peptide chain. Polarized infrared radiation studies of keratin show rather low dichroism. They suggest that keratin must contain considerable regions of unknown structure as well as regions where the α helix structure predominates.

The evidence in support of the α helix and β pleated sheet structures as dominant features of the α and β fibrous protein structure is in general diverse and formidable. Existence of the α helix structure has been clearly demonstrated in some synthetic polypeptides.

References

There are several recent accounts of work on fibrous proteins and on polypeptide chain configurations. Some of these are listed below. The original papers by Pauling and Corey describing the α helix structure and the pleated sheet β configurations are also listed.

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Pauling, L., Corey, R. B. and Branson, H. R. Proc. Nat. Acad. Sci. U. S., **37**, 205 (1951).

The next paper is entitled "The Structure of Feather Keratin." It is by Dr. S. Krimm, who is Assistant Professor of the Physics Department at the University of Michigan, working with Professor G. B. M. Sutherland, who is well known for his work in Infrared Studies on Proteins.

THE STRUCTURE OF FEATHER KERATIN

SAMUEL KRIMM

Department of Physics, University of Michigan

I am going to present to you this morning some preliminary ideas on the structure of feather keratin. After the beautiful introduction and general discussion given by Dr. Low, I am sure that my task will be immensely easier. I will be dealing with the same type of problem that she has discussed, namely the configuration of a protein in terms of its constituent polypeptide chains. It hardly needs to be said in this connection that the structure of feather keratin is not only of interest in itself but also in relation to the entire question of the structure of proteins. This is especially true since a satisfactory structure in terms of the models proposed by Pauling and Corey has not yet been achieved for this protein. The solution of this structural problem is therefore, in a sense, a test of the principles and assumptions which have been used thus far in deducing the configurations of proteins.

Let us consider first the historical background of the problem. The X-ray diffraction pattern of feather keratin indicates that the structure is related to that of the β proteins, i.e., that the polypeptide chains are in the extended form. This conclusion is derived mainly from the presence of a 3.08 A meridian spacing, which is to be compared with 3.3 A in stretched hair and 3.5 A in silk, both of which are known to be β proteins. While the general features of the diffraction pattern of feather indicate the presence of extended polypeptide chains, there are certain aspects which show that the configuration is more compli-

cated than the usual sheet-like array of extended chains thought to be characteristic of β proteins. One of these is the large fiber axis identity period of 95 A, with its pronounced 4th order at 23.7 A. This cannot be directly correlated with the repeat of a simple extended polypeptide chain, which is about 7 A. Furthermore, the large equatorial spacing of about 33 A shows that the fundamental separation between units, in a direction perpendicular to the fiber axis, differs from the usual 10 A separation between sheets of the ordinary β type. And finally, although it has been found possible to stretch feather quill by about 6%, and thereby increase the 3.08 A meridian spacing to a value almost equal to that in stretched hair, we have found that the diffraction pattern does not resemble that of the ordinary β protein but still retains its original detail. These features indicate that the structure of feather keratin, while probably based on extended polypeptide chains, is not of the simple sheet type found in the usual β proteins.

Some efforts have been made to alter the diffraction pattern by means of chemical treatment of the feather, and thereby gain some clues about structural changes. For example, feather has been treated with mercuric acetate, which presumably breaks cystine bonds and introduces mercury into the structure. The only result of this treatment, however, seems to be an enhancement in the intensity of the 11.9 A meridian reflection. Of particular interest to us at present are the results of the treatment of feather with various types of solvents, such as hot water or alcohol. In this work Bear found that although much of the diffraction pattern might be destroyed by the treatment, certain features remained essentially unaffected, in particular the strong 4th order meridian spot at 23.7 A. On the basis of this and other considerations, Bear has suggested a micellar type of structure for feather keratin. According to this interpretation, the long spacings in the diffraction pattern arise from the large size of the micelles, or particles, along the fiber axis direction, while the short spacings are related to the intra-particle polypeptide chain configuration. We will consider this structure in more detail later.

Subsequent proposals for the structure of feather keratin have been based on the α-helix polypeptide model of Pauling and Corey. In their first proposed structure, these authors suggested a model consisting of alternate layers of α-helices and extended polypeptide chains. We may designate this as a composite structure, i.e., one made up of more than one type of structural component, in this case an α-helix and an extended chain. Although this model did explain some aspects of the X-ray diffraction pattern, it did not account for many other important features. For example, it would require the presence of a 1.5 A meridian spacing, which is not found, and it results in predicted X-ray intensities which are not in agreement with those observed. For these reasons this structure has been discarded.

Pauling has proposed a second structure based on a coiled α-helix. Crick had observed that if two α-helices were required to pack together

most efficiently, they would do so by twisting about each other, such as do the strands in a rope. Pauling has suggested a similar type of coiled structure for feather keratin, one in which six α-helices twist about a central straight α-helix. This structure, however, is not considered to be satisfactory since it also does not give good agreement with the observed X-ray intensities. Furthermore, it would not give results in agreement with the observed infrared dichroism of feather.

We might consider for a moment the phenomenon of infrared dichroism, since we are using it as a criterion for an acceptable structure. If an infrared absorption band is related to a vibration in a specific chemical group, such as N—H, then the orientation of such a group in the molecule can, in general, be determined by the use of polarized infrared radiation. This is possible because maximum absorption of the radiation will occur when the electric vector in the polarized beam coincides in direction with the change in dipole moment in the vibrating group. Thus, for example, we would expect that, since the N—H groups in an α-helix are oriented essentially parallel to the axis of the helix, the maximum absorption for the N—H frequency should occur when the electric vector is oriented parallel to the fiber axis. As a matter of fact, for feather maximum absorption occurs when the electric vector is perpendicular to the fiber axis, and this is sufficient to exclude the proposed coiled coil model of feather keratin.

We may finally note that for the usual type of β protein, in which the extended chains are aggregated by means of hydrogen bonding into sheets, one finds an additional characteristic fiber axis spacing of about 1.15 A. This corresponds to an enhanced 6th order of the extended chain identity period of about 7 A, and is strong because of the near regularity in the interval between successive atoms along the main polypeptide chain. No such comparable spacing has been observed in the diffraction pattern of feather, and this again leads one to believe that the structure of this protein must involve some variation on the simple idea of a linear extended chain.

Before discussing our recent ideas on the structure of feather, I would like to describe the results of some experiments we have done which are pertinent to this problem. We have examined, in greater detail than done by previous workers, the effects of stretching on the X-ray diffraction pattern of feather. Astbury had reported an increase in the 3.08 A spacing when feather quill is stretched. The following table shows the changes which we have found in other meridian spacings when feather quill is stretched at room temperature and humidity. These results show that within experimental error all of the meridian spacings increase by the same relative amount. At the same time we observed essentially no change in the equatorial spacings. And finally it may be noted that the stretching does not appear to be accompanied by any significant change in the relative intensities of the spots in the diffraction pattern. Thus, on stretching feather quill, the only significant change in the diffraction pattern is a uni-

form increase in all of the fiber axis spacings. The elongation of the sample and the corresponding change in spacings are continuous and essentially reversible. The only limitation is that an extension of greater than about 6% appears to be impossible: the sample invariably breaks.

These results appear to lead to the following conclusions. The structure is capable of a definite but limited extension along the fiber axis direction. This is indicated by the increase in spacings on stretching and the limitation to elongations no greater than about 6%. Furthermore, the general configuration seems to be basically unaltered by the elongation, since the nature of the pattern and the relative intensities remain essentially the same. These results appear in particular to exclude a particle type of structure, because in this case we would not necessarily expect that large and small spacings would change by the same percentage. This might happen, of course, if the inter-particle

TABLE I

CHANGE IN MERIDIAN SPACINGS OF FEATHER QUILL ON STRETCHING

Before	After	Percent elongation
3.08	3.23	4.87
4.985	5.225	4.81
6.300	6.620	4.83
23.60	24.75	4.87

binding were as strong as the intra-particle binding, but if this were so it is then not clear what meaning could be attached to the term "particle." Finally, it appears that a composite type of structure is not in harmony with the above stretching results. Not only might we expect that both components would not extend proportionally the same upon sample elongation, but there is no evidence that a structure such as an α-helix could remain stable upon a 6% axial elongation. Thus, the evidence seems to favor a homogeneous type of structure, i.e., one built up from a single type of chain configuration. Assuming this to be the case, we may turn now to the structural implications of the infrared spectrum of feather.

Although the X-ray diffraction pattern of feather indicates that it is a very highly oriented structure, it is significant that the numerical value of the dichroic ratio is nevertheless small. The dichroic ratio, taken as the ratio of optical density for radiation polarized perpendicular to the fiber axis to that for parallel polarized radiation, is about 1.3 for the NH and CO stretching bands. This is to be compared with the values of about 2.7 for silk and 3 to 4 for synthetic β polypeptides and nylon. The low dichroic ratio might result from the presence of amorphous material, but there is no indication from the diffraction pattern of any significant amount of such disordered regions. A combination of α-helices and extended chains could, of course, also account for this fact, but as we have seen there are good reasons for rejecting

a composite type of structure. It therefore seems that we must consider the low infrared dichroism to be a significant structural feature. In particular, if we assume a homogeneous type of chain configuration then the dichroic ratio must be directly related to the average chain orientation.

Assuming a random orientation of the CO and NH groups about the fiber axis, which is valid since the X-ray pattern is cylindrically symmetric, we find that the numerical value of the dichroic ratio implies that these groups make an average angle of about 60° with the fiber axis. Since the group is approximately perpendicular to the local chain axis, we may say that the average local chain direction makes an angle of about 30° with the fiber axis, probably plus or minus a few degrees. This distribution of dipoles does not, of course, automatically define the chain configuration; this must be arrived at from other considerations. We have postulated, as a reasonable model which will account for these results, a chain configuration which is helical, with an angle of about 30° between the chain direction and the helix axis. This is perhaps not too unreasonable in view of the presence in the chain of 10-11% of proline residues, which might be expected to cause a deviation (presumably always in the same sense) from the usual linear direction of an extended polypeptide chain. The structure to be developed on this basis must, of course, be considered as tentative at the present stage. Its validity will be determined by the extent of agreement between prediction and observation.

We may proceed now to characterize this structure in greater detail. In order to completely define the helical structure, we must give not only the helix angle but also either the radius or the pitch of the helix. Although there is at present no independent basis for determining these quantities, the following arguments yield plausible values. We will show shortly that the helical chains will tend to aggregate in an array which forms essentially a hollow cylinder. Therefore the radius of a single helical chain must be large enough so that side chains may be accommodated within the cylindrical structure. In the usual β proteins the sheets of polypeptide chains are separated by about 10 A in order to accommodate side chains and we would therefore expect the diameter of the cylinder to be somewhat larger than this. At the same time it seems natural to try to account for the long fiber axis repeat in terms of the pitch of such a helical chain. If we assume the pitch to be 95 A, to coincide with the long fiber axis repeat found in the diffraction pattern, then the diameter of the cylindrical aggregate is found to be about 17.5 A, which would satisfy the requirement for packing of side chains. On the basis of this structure the 3.08 A meridian spacing results essentially from the projection of the individual residues onto the helix axis. This requires a residue length along the chain of 3.55 A, a not unreasonable value. It might be remarked that if the internal side chains are small, so that the helix radius need not be so large, a possible structure could have a pitch of

47.5 A and a chain angle a few degrees larger than 30°. Although we intend to investigate this possibility, we have chosen to examine the former model in detail at present.

We have mentioned that individual helical chains will tend to aggregate to form a larger unit. This is a result of the tendency of the system to form the maximum possible number of hydrogen bonds. If we assume that neighboring chains will be hydrogen-bonded to each other at the usual distance of about 4.75 A, then we find that this can be achieved by arranging helical chains coaxial with each other and separated by a fiber axis translation of 9.5 A. We see immediately that this will permit ten chains to fit into the 95 A fiber axis identity period. The entire unit, which is shown schematically in Figure 1, thus approximates to a hollow cylinder, with the main chains forming the surface of the cylinder and the side chains projecting both inside and out. The density of such a structure is satisfactory. One bad feature might be the large hole down the center which remains even after taking into account the space occupied by side chains. It must be noted, however, that the constraints on the system, such as for example the proline in the chain, may result in the assumption of such a configuration even though the overall packing of chains is not the most favorable. We are, however, also considering the possibility that the 47.5 A pitch helix may account for these features in a somewhat more satisfactory manner.

The question immediately arises as to whether this model accounts for the main features of the X-ray diffraction pattern. We have not yet examined this in detail, except for the equatorial reflections. Figure 2 shows a possible reasonable way in which these cylindrical "molecules" might pack. We assume that seven of the cylinders form a somewhat stable configuration, with these larger units forming a hexagonally close-packed array. The individual cylinder has a diameter of about 22.3 A, to allow for the projecting side chains, and therefore the unit cell is hexagonal with $a_o = 67$ A. By considering the keratin molecule as approximately a hollow cylinder, we calculate the following equatorial spacings and intensities. Although the agreement is not completely satisfactory, undoubtedly in part a consequence of choosing an over-simplified model, the structure does seem to account for the general trend of the strong and weak reflections. In any event, the agreement does not seem to be bad enough to invalidate the general type of structure. We will expect, of course, that the agreement should improve with further refinements in the model.

The problem of the meridian reflections is a more difficult one, especially since at this stage no exact atomic coordinates have been specified. It will be useful, however, to inquire into the possible implications of the dominant 23.7 A meridian spacing. This strong and persistent spacing implies that the 95 A fiber axis period is characteristically divided by four unique regions of electron density. I am proposing that these regions contain the proline residues. In other words, each helical chain has four proline residues equally spaced in

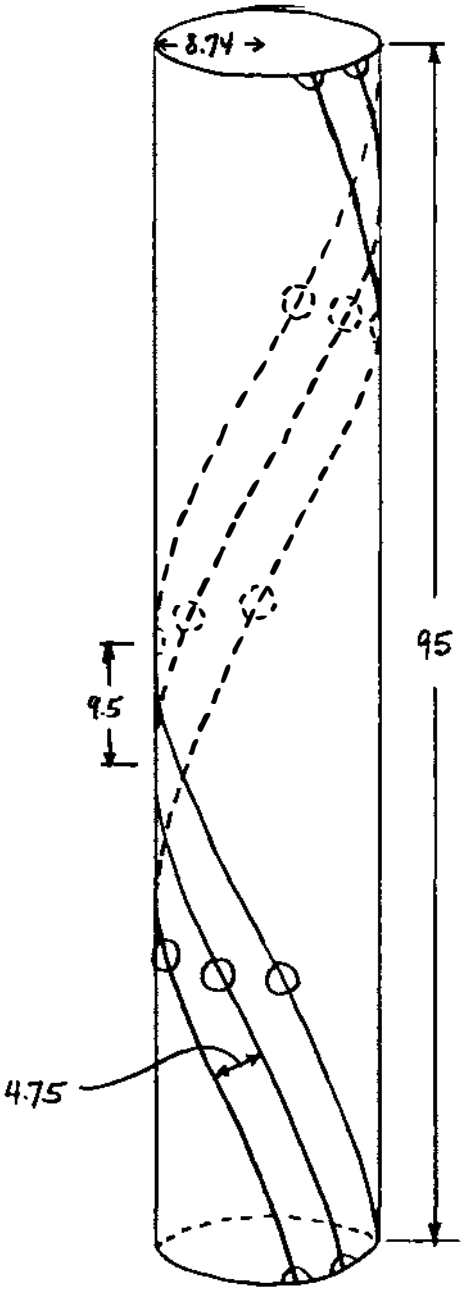


FIGURE 1

Model for feather keratin structure.

Only 3 of the 10 chains are shown. Hydrogen bonding takes place between chains separated by 4.75 A. Side chains project into and out of the cylinder. Small circles represent proline residues, shown as congregating at particular levels.

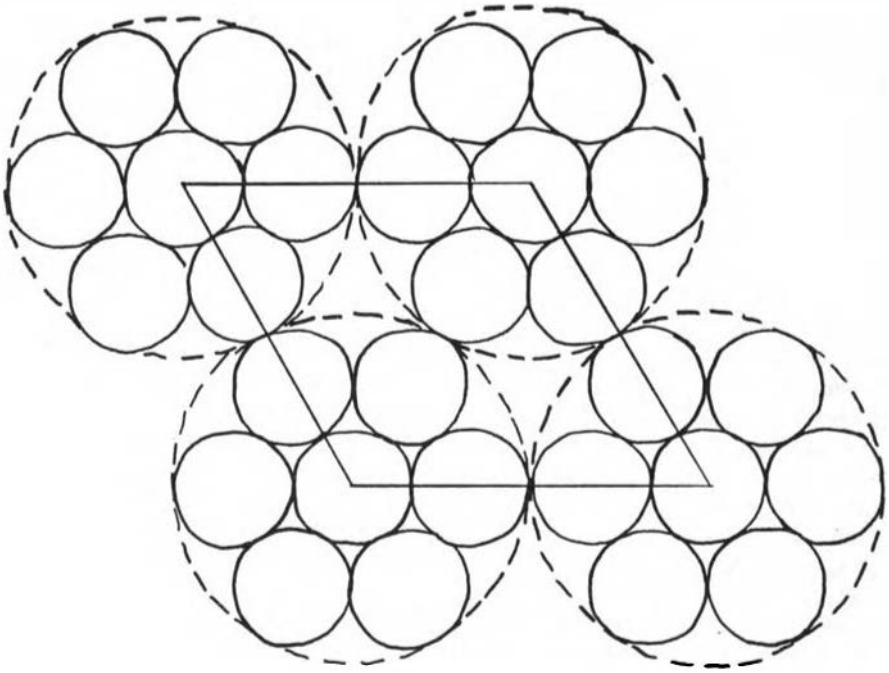


FIGURE 2

Packing of feather keratin molecules.

Each small circle represents the cross-sectional view of the molecular envelope of a unit such as that in Fig. 1. The hexagonal unit cell has $a_o = 67$ A.

the 95 A repeat, and the proline residues of the ten neighboring chains in the cylindrical array tend to congregate near the same level. The required residue percent of proline on this basis is 12.9%, not too far from the 11% which is found. The discrepancy is not too serious, since the disordered regions of the feather may contain less proline than the crystalline portions. If the polypeptide chain tends to bend

TABLE II

EQUATORIAL SPACINGS FOR PROPOSED MODEL OF FEATHER KERATIN

Index		Calculated		Observed	
h	k	Spacing	Intensity	Spacing	Intensity
1	0	58.0	0.677	55	m
2	0	29.0	0.144	—	—
3	0	19.4	0.470	—	—
6	0	9.65	0.60	—	—
12	0	4.83	2.94	~ 4.7	ms
1	1	33.5	1.05	33.5	s
2	2	16.8	0.27	17.1	w
3	3	11.2	4.95	11.2	s
4	4	8.38	0.092	8.7	m
6	1	8.85	0.003		

or change direction at a proline residue, then it is not unlikely that the best fit of chains will be achieved when the bends occur at about the same level. Furthermore, since no hydrogen bonding can take place with the proline N, it would be more favorable to group the prolines together, thus permitting the other portions of the chain to enter into bonding. Otherwise, if the prolines in neighboring chains were randomly distributed with respect to each other, a larger number of hydrogen bonds would be prevented from forming. Although this explanation accounts for a strong 4th order in terms of the nature of the side chain distribution, this may not be unreasonable since the proline is rigidly fixed to the chain and should therefore give rise to greater coherence in the scattering than do the other types of side chains. It may be noted that if the other residues are similarly located at about the same level, we would expect, as is found, a strong meridian spacing of 3.08 A. We can now readily see that a structure such as the one proposed would indeed have the definite but limited extensibility which is observed. To elongate this structure by 5% requires a 1° change in pitch angle. This should be quite feasible without changing the overall general configuration, thus accounting for the unaltered relative intensities on stretching. It is perhaps also of interest, although it may be fortuitous, that when feather keratin is solubilized it is possible to obtain units of molecular weight about 34,000 whose size, in terms of a cylindrical shape, is approximately 97 A by 23 A. The molecular weight of a 95 A long segment of our keratin structure, whose diameter is about 22 A, is 34,100. Too much emphasis need not be placed on these figures, but they are suggestive.

In conclusion, I wish to reiterate that these represent some rather preliminary and tentative ideas on the structure of feather keratin. Whether this structure will prove to be "correct" will depend on how well it bears the burden of further more detailed examination. In particular, we hope to check it by building molecular models and by examining the cylindrical Patterson function. These should provide specific and perhaps conclusive tests for the model.

CHAIRMAN SCHUBERT:

We have had three extremely interesting papers this morning and I am sure that there are questions which some of you desire to ask the authors. I would appreciate it if the authors would come to the front seats so as to facilitate the answering of questions. This request includes Dr. Kennedy as some questions will be addressed to him.

Discussion

QUESTION:

How was the infrared spectrum obtained?

DR. KRIMM:

By placing sections of a piece of quill in a spectrometer.

QUESTION:

Do you have the references to this work?

DR. KRIMM:

Not at the moment, but it was done primarily by the Courtaulds group. I might say that the specimen is in the solid state, and has to be very thin, perhaps 5 to 10 microns.

MR. LERMAN:

In feather keratin, would anybody venture a guess as to the percentage of an amorphous versus crystalline material, since that would have a very important bearing on modification of the structure and its properties.

DR. KRIMM:

Although I don't have any quantitative data, I am sure that the amount of amorphous material must be fairly low. This is because the diffraction pattern does not show much of the diffused scattering which is due to amorphous material. If there were an appreciable amount present, it would of course affect the dipole orientation angle determined from the infrared, but I have assumed that this is not the case.

QUESTION:

Did I understand the CO and NH frequencies were somewhat different?

DR. KRIMM:

The actual values of the dichroic ratios in the case of feather are nearly the same. The difference does not seem to be as large as is true for the α proteins. The dipole orientation angles calculated from the two dichroic ratios in the case of feather differ only by about 1°.

DR. LOLLAR:

I'd like to pursue this amorphous versus crystalline regions question. Thinking from the planar array of the peptide chain, and the fixed bond and fixed angles, what leads us into the amorphous region rather than to the ordered regions? Does anybody wish to discuss it?

PROFESSOR BEAR:

I don't think I have any answer. I agree there is not very much diffraction evidence. We have not been as quantitative as we should have been in this system, yet comparing the diffraction pattern with any background, I want to make a case for the micella type of molecule. I don't think we had the very nice results presented by the stretchings. That does not necessarily mean we can't have them. All of the spacings moving there are really smaller than the size of the molecules, we expect. In recent years, there has been accumulating evidence that feathers can be dissolved in reagents by oxidation, and one gets a surprisingly homogeneous population of molecules. This has a molecular weight of 110,000 and was confirmed in two different labs by about a half dozen different methods. In our lab, the construction isn't perfect but the surprising thing to us was the thirty-four angstroms. Chemistry has a hard time seeing why this should be so, unless one dimension is thirty-four. There looks to be another one about a hundred, so we have come to the tentative solution that the

monomer, instead of being the elliptical particle you say, looks like a sheet, a little rectangle, rather thin—thirty-four this way and a hundred the other way. This is surprising itself, and if this is the proper way to look at the particle, we must look at three polypeptide chains; and, in connection with this twisting business, one doesn't know as yet whether the chains would all have to be twisted at one phase to which they have gone, or whether this might be done several times through there—and many times would look like amorphous material.

DR. LOLLAR:

It would seem to me that would imply a relatively low amorphous region. The chain corners wouldn't look like enough amorphous regions to explain high levels.

DR. STAHL:

All of ourX-ray analyses are on such things; for example, the X-ray analysis on the rachis portions. However, we know that morphologically the rachis is probably not an individual material. For example, Lundgren at Western Regional has been able to take feather keratin and, by means of enzymes, to dissolve it into two distinct cellular components (spindle and polygonal cells).

DR. KRIMM:

That is a very important point, of course—whether the rachis is homogeneous. Did you say that Lundgren had found two distinct types?

DR. STAHL:

This is a point we have not settled. They have sent a letter and photographs to Dr. Kennedy, and they are of intense interest to us; I would suppose to you, also. Dr. Corey at the present time is going to intensively investigate this problem.

DR. KRIMM:

We tried testing this in a rather crude way. We sectioned a piece of quill lengthwise into four parts. We found that each section gave the same X-ray diffraction pattern, thus seemingly indicating that the quill is homogeneous across its thickness. It is perhaps of interest in this connection that we have found the X-ray diffraction pattern of the quill near the tip of the feather to be different from that further from the tip. In particular, the very tip gives a disordered pattern. About 2 to 4 mm. from the tip one finds the usual diffraction pattern, but oriented at right angles to the quill axis. From here one goes through a region of intermediate orientation, until, at about 1.5 cm. from the tip, the feather pattern is oriented with its fiber axis along the quill axis. This tends to indicate that some particular structure is being extruded and then oriented.

DR. LOLLAR:

One additional question on splitting the quill in four parts—did it go through the pith area?

DR. KRIMM:

No, we only took sections of the quill wall.

QUESTION:

Has there been any work done on the differentiation between the goose and the duck, and different species of the two?

DR. STAHL:

The amino acids of the duck feathers are different from those of the goose. There have been no complete amino acid analyses between the goose and the duck. There has been an analysis of the cystine and myosin contents between the two, and these differ by a percentage that exceeds ten percent. So, this is again in line with our observation that there exists, between species, a difference. What this will mean to the X-ray people, I don't know.

QUESTION:

Has any work been done on different species of geese?

DR. STAHL:

No, no studies on varieties. Until we are absolutely positive of species difference, there is no use to look for a variety difference within a species.

DR. LOW:

Two questions to Dr. Krimm. In considering the chains, as twisting together to form the large helix, it seems to me you must have had some sort of pleated sheet. You must have chosen some specific configuration. I wonder what it looks like. Did you put in the β carbon atom position in all the residues when calculating intensities? And, lastly, when you say the density of this model fits when you pack all the seven chains together what is the density of this structure? It always seems to me that the problem of gross density is a very difficult one to cope with.

DR. KRIMM:

You are touching on very important points, which, unfortunately, we have not yet had the chance to go into in detail. Until one builds a model it is rather difficult to be specific about the polypeptide chain configuration. I am assuming that it is very close to one of the variations of a fully extended chain, such as have been discussed by Pauling. We cannot, therefore, at present specify exact coordinates. My feeling has been that one could build a model to fit the requirements. I may be wrong on that, but we will know more certainly when we try.

Since we do not as yet have exact atomic coordinates, we have not made any detailed intensity calculations. However, it does seem that if one were to choose any residue which could contribute most coherently to the scattering, one would choose proline because of its relatively fixed position in the chain.

The density of the total structure is a little bit lower than it ought to be. It is 1.1, and should be about 1.28. It may be that the structure could in this sense be more satisfactorily built up from the 47.5 A pitch helices. The difficulty here seems to be that the cylindrical unit is then not large enough to allow for the side chains. These are all very definite problems which we hope to clarify by future work.

DR. SCHUBERT:

There was a little difference of opinion as to whether there should be discussions after each paper or as we are doing. I believe that we are having a better discussion by handling it this way. Are there any further questions?

MR. ARMSTRONG:

If you were to measure the amino acid content of pigmented feathers, and I presume many are, would you expect appreciable differences from the white?

DR. STAHL:

I think I would answer that by saying if one calculates these on the basis of the number of amino acid residues present rather than percent weight of the total material, that you will get a truer picture of amino acid content. Carbohydrate might be there, or pigmented material. The amount of this material is exceedingly small. I doubt if it exceeds five percent of the total weight. This has not been corroborated.

MR. ARMSTRONG:

In wool, it's been shown pigment consists to a greater extent of basic amino acids than protein, and this raises the question, since we're interested in the practical end result of this work, that these fine differences will influence this. I suspect a process will influence a pigmented fiber differently than a white one. Now, regarding the copper treatment of feathers, there was an indication that the copper did react with every cystine. The mercury did not react with every cystine, but every fourth one. You mentioned something about mercury reacting with the feather keratin, and you made the point it didn't react with every cystine.

DR. KRIMM:

My point was that it did not significantly alter the intensities of any of the reflections except the 8th order.

MR. ARMSTRONG:

I guess in my own mind I said that, and it's well known the cystines are not alike in wool and might be true in feathers.

DR. KRIMM:

If all the prolines were exactly in the same horizontal plane you would predict a certain intensity variation in the 4th, 8th, and 12th orders. If neighboring prolines were successively displaced from this plane, there would be a stronger diminution in the intensities of the higher orders. It is possible that, when the S–S linkages are broken, there is a slight change in the relative translation between neighboring chains which leads in this way to the observed intensity changes.

DR. STAHL:

You recall I mentioned that if we took feathers apart into these four histological parts, that there were distinctly different cystine contents to these parts. This information is a gross analysis, and doesn't allow us in any way to determine which ways it is tied up in the molecules; but, they are different in anatomical parts.

DR. MACKAY:

I'd like to ask Dr. Krimm whether he considers his model typical; and, second, although feather keratin cannot be extended, has anyone tried to do the equivalent of the beta-alpha conversion that can occur in wool and hair by contracting feathers?

DR. KRIMM:

I don't believe that this type of model is general for all β proteins. The ordinary sheet structure of extended chains certainly seems to be satisfactory for silk and stretched hair. The present model may be a special one arising as a result of the proline in the chain. It does seem to fit the X-ray diffraction pattern and infrared spectrum better than the usual β structure.

DR. STAHL:

Mr. D'Antonio will show you where he's been able to shrink feathers on the order of ten percent.

DR. MACKAY:

Would your model allow for a contraction?

DR. KRIMM:

I would expect that the structure would allow for a contraction of about the same order of magnitude as the extension, namely about 5%.

QUESTION:

I'd like to inquire of Dr. Krimm—he talks about extension; in relation to what part of the feather—the whole quill or just part? You're talking about extension?

DR. KRIMM:

Our extensions are done on a small piece of quill, perhaps 1.5 cm. long and 1 mm. wide. We just put this in a vise and slowly pull on it.

QUESTION:

We've found it makes a big difference what part of the quill you take. Of course, it has a variable diameter. Diameter is very important. You find you get bad slippage which causes variability. You find that, with much stretching close to the tip, the elongation is much different than if you take the part of the quill two or three centimeters from the end. In the work we've done, we've tried to get the same diameter from the top and bottom.

DR. KRIMM:

We always choose the specimen from that part of the quill which gives the well-oriented and definitive X-ray diffraction pattern. If the sample breaks after say 2% elongation, we assume that it was an unsatisfactory specimen, and we try another.

COMMENT:

We've found a tremendous variation in feathers. You can't get representative results at any time. Three percent is as far as you can go without degrading the feather in any way.

TECHNICAL SESSION NO. 2

DR. ADOLF SCHUBERT, *presiding*

CHAIRMAN DR. A. SCHUBERT:

We will now have a paper by Dr. J. D. Loconti, who is the head of the High Polymer Section of the Pioneering Research Division of the QM Research and Development Command here at Natick.

Dr. Loconti will speak on "The Morphology of Feathers And Down."

THE MORPHOLOGY OF FEATHERS AND DOWN

J. D. LOCONTI

Pioneering Research Division, Quartermaster Research and Development Command

In conducting a search for a substitute filler for sleeping bags we have first asked ourselves the question, "What properties or what characteristics of down are responsible for its effectiveness as a filler and insulator?" To answer this question we have instituted a broad program of research on feather keratin, its chemistry, its amino acid composition and sequence and its molecular structure; on the gross structure or morphology of feathers and down; on the moisture sorption behavior, on the characterization of associated fatty substances, on single fiber properties and on the alteration of feather structure by chemical means.

Much of this work is being done in the Pioneering Research Division here and some by Drs. Corey and Schroeder at California Institute of Technology and Drs. Sutherland, Krimm and Wood at the University of Michigan. Dr. Stahl and Dr. Krimm have already reported on part of this work.

What we would like to report in this paper and one of the following papers by Mr. D'Antonio are the results of our studies on the geometry of feathers and down, and the effect of the number of chemical treatments on the detailed changes in the geometry of the chicken feathers.

If one compares down, a good filler and insulator, with feathers, which are much inferior in these qualities, the most obvious difference is in the geometry. It was appreciated from the beginning that this was perhaps the over-riding characteristic which gave down its unique properties. Our studies appear to bear this out.

I would first like to show the structural features of eider down, duck feathers and chicken feathers, by a series of photo micrographs, taken by Mr. Wrigley and Mrs. Hynek of our Microscopy Section. They reveal very significant differences to which we are attributing much of down's superior bulking capacity.

Figure 1 shows a cluster of eider down. The thickened basal portion

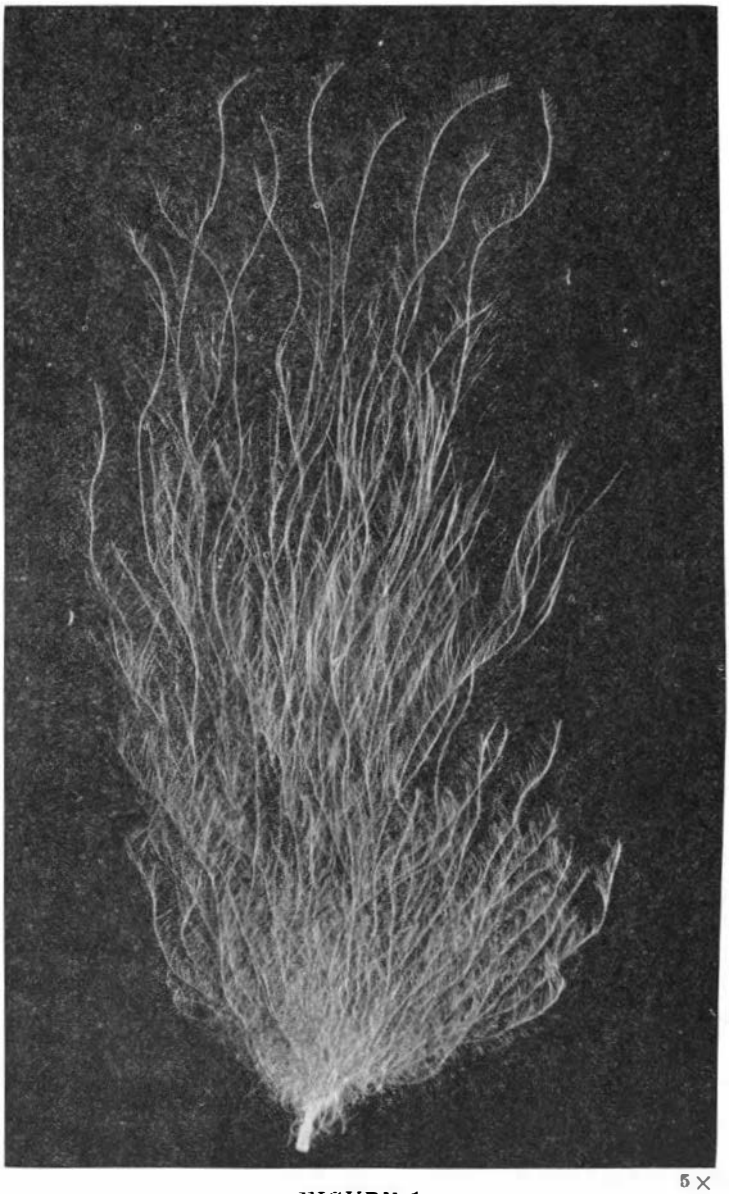


FIGURE 1
Eider down.

is called the body attachment, the point at which the down cluster is attached to the bird. The long fibers are called filaments and the short branches are called fibrillae. You'll note that the filaments radiate out from the body attachment in all directions. This particular sample was combed out, but, in the natural state, down is a cluster looking something like a ball. This gives three-dimensionality and good space-filling characteristics.

One of these filaments is shown enlarged in Figure 2. The picture at the left shows a portion of the axis of the filament with the radiating fibrilla. The triangular swellings at the ends are called trows. The picture at the right shows the axis of a filament at 324 diameters, and you will notice the fibrillae curve around the axis before branching out. The branching occurs in any plane passing through the axis, giving the filament an effective cylindrical structure. You will see later where this structure's space-filling capacity is a very important factor in the bulking capacity of down.

Figure 3 shows the fibrillae at greater magnification; note the prongs. It's quite likely these portions of the structure play an important part in the ability of down to resist compression and matting, and also its ability to refluff readily.

Figure 4a shows a duck feather at the left. I'll repeat what Dr. Stahl stated about the major component parts. The main stem of the duck feather is the rachis and the main branches are barbs. The barbs at the top of the feather are called vane barbs which form a continuous flat structure. The barbs of the lower half of the feather are fluff barbs. All barbs emerge from opposite sides of the rachis to give a flat or two-dimensional structure. A plane will pass through the barbs on each side, and the rachis, too. There is some deviation from planarity due to some curl and various degrees of fluffiness, but, by-and-large, it is fundamentally flat, in contrast to the three-dimensional structure of down.

Figure 4b shows a fluff barb at high magnification. The branches are called barbules. This structure is almost exactly like the feather. The main stem is analogous to the rachis and the barbules are the counterparts of the barbs. They lie in a single plane so again we have a two-dimensional structure just like the parent feather.

Figure 5a shows a single fluff barbule revealing the swellings called trows at the end of the axis. Figure 5b shows the trows at still higher magnification.

Figure 6a shows a vane barb of a duck feather. Here we have a much more compact structure. The barbules are much shorter, so that its space-filling capacity is very limited. They also emerge from opposite sides of the axis, and consequently have the two-dimensional overall structure. The barbules are shown in figure 6b. The one at the right is an outer vane barbule and on the left is an inner vane barbule.

Figure 7 shows a greatly magnified picture of the hooklets of a vane feather barbule. They are very effective in maintaining the flat, vane

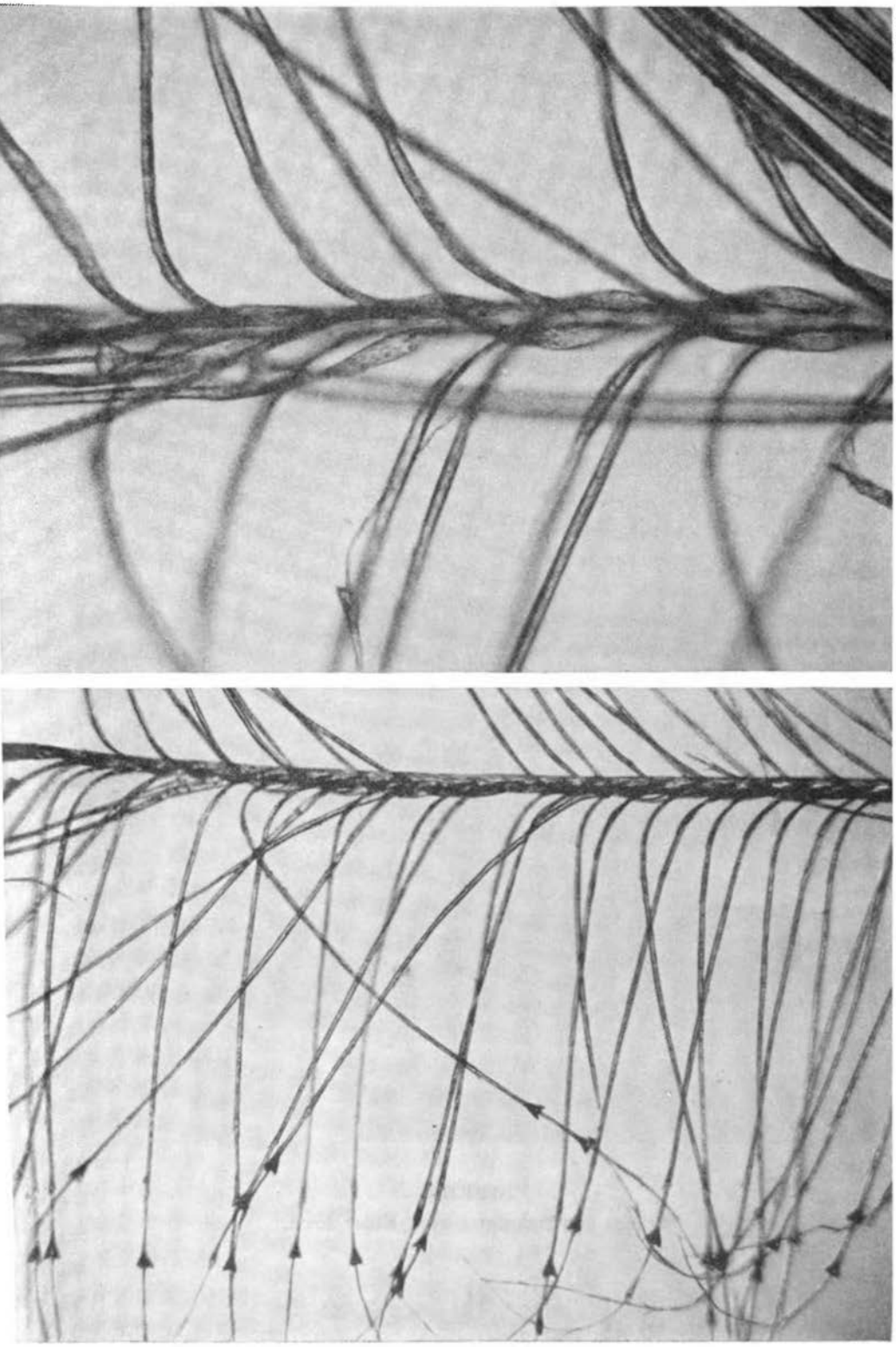
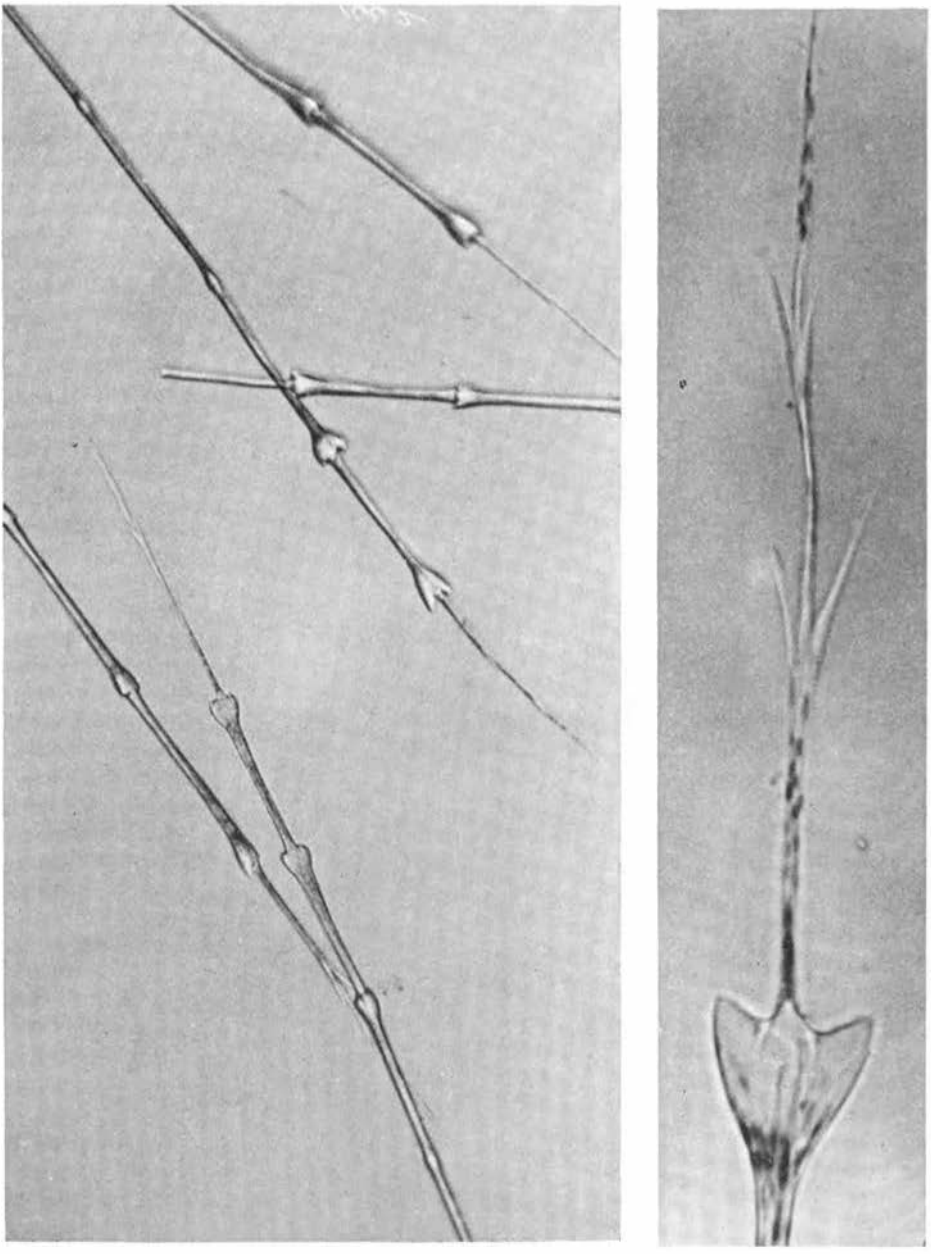


FIGURE 2
Eider down filaments.

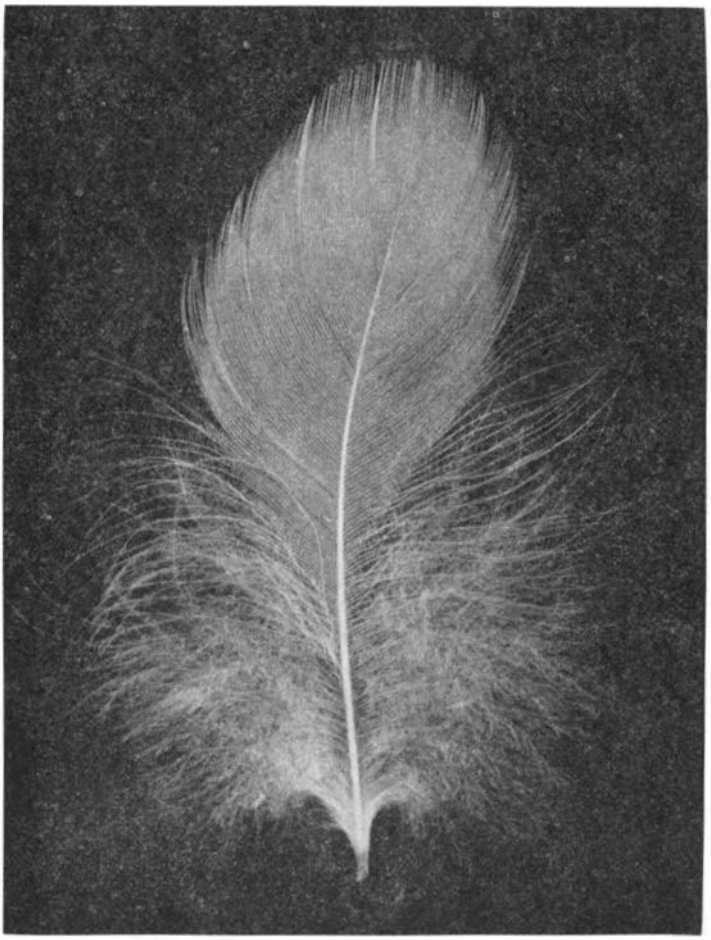


277 ×

1270 ×

FIGURE 3

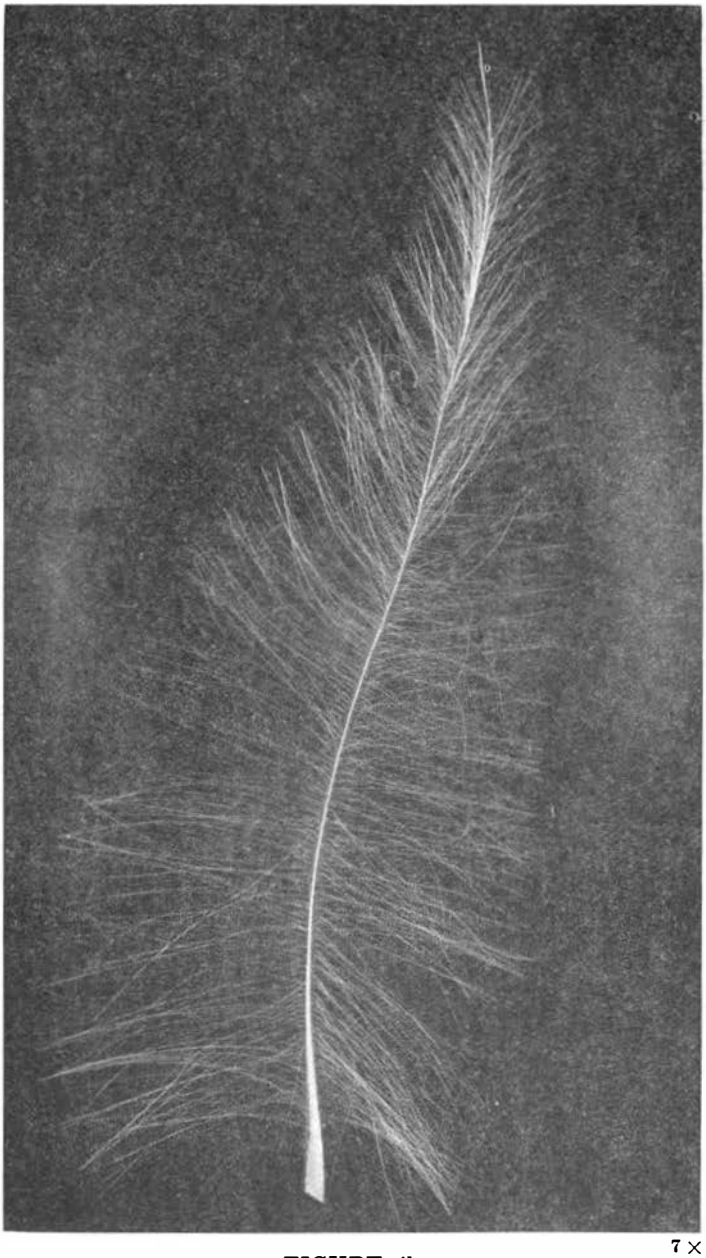
Prongs and nodes or trows; Eider down.



2 ×

FIGURE 4a

Duck feather.



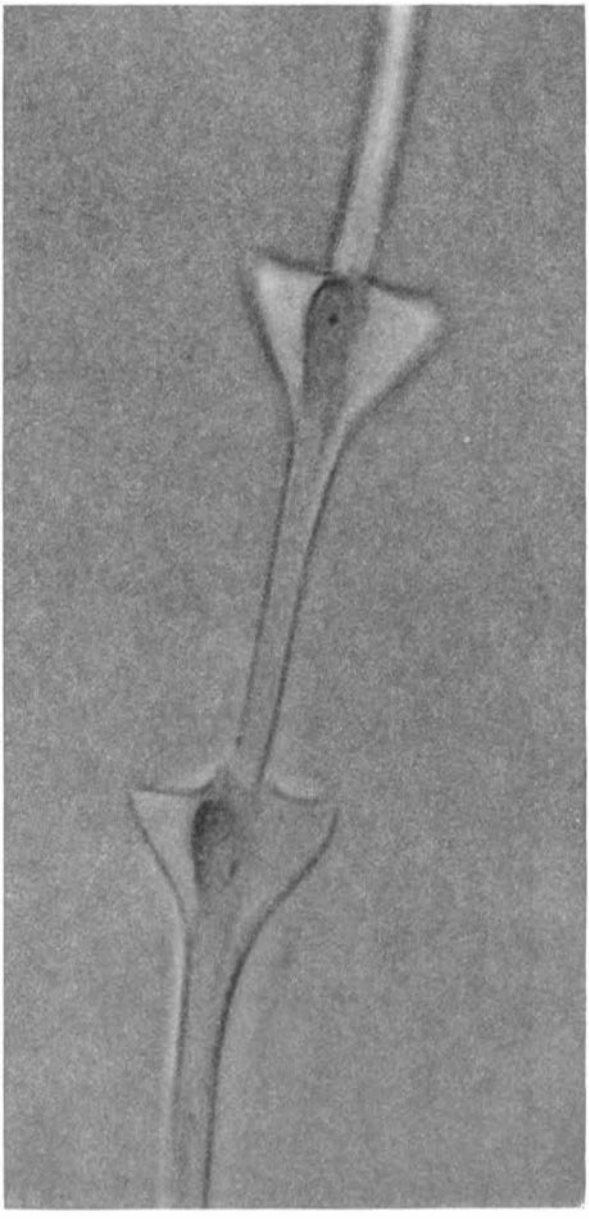
7×

FIGURE 4b

Fluff barb.

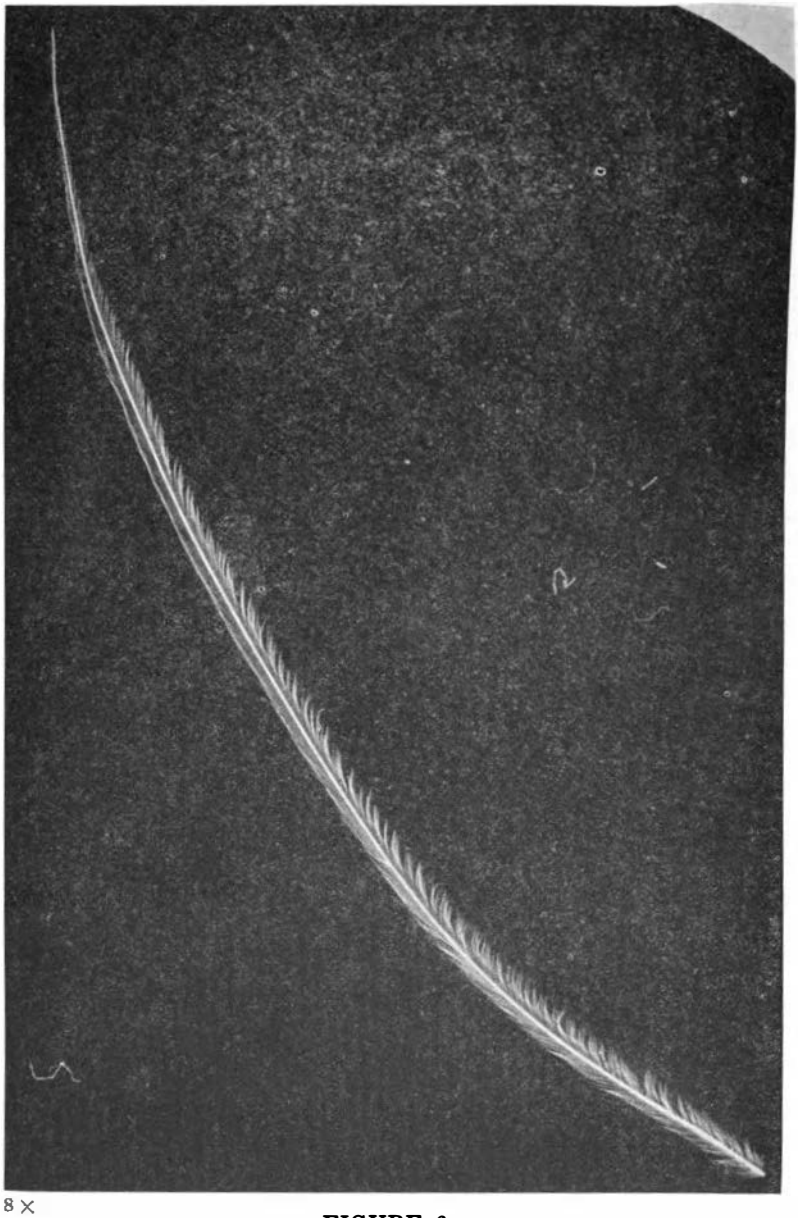
255 ×

FIGURE 5a
Fluff barbules.



1295 ×

FIGURE 5b
Trows.



8 ×

FIGURE 6a

Vane barb.

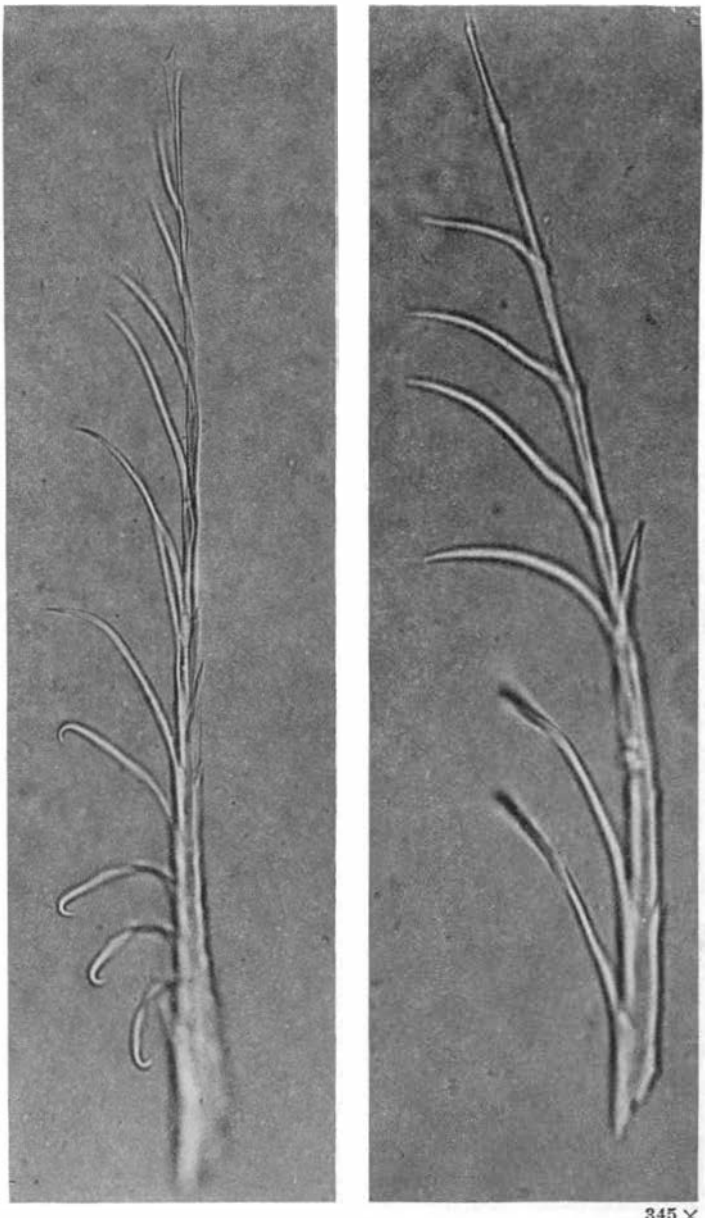
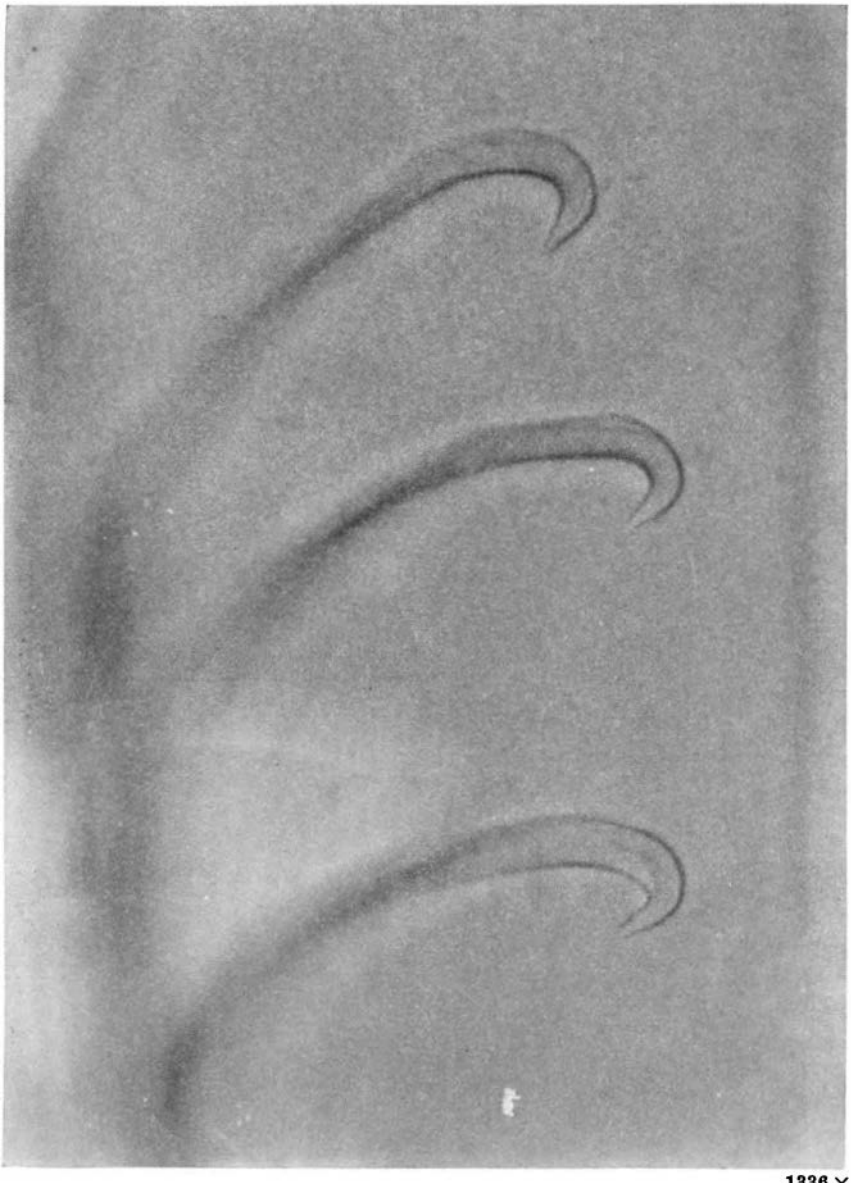


FIGURE 6b

Vane barbules.



1336 ×

FIGURE 7

Hooklets.

feather structure and consequently are an important factor in reducing the bulking capacity of feathers.

Figure 8a shows a typical chicken feather with its part vane and part fluff structure. Figure 8b shows the partly stretched vane portion showing how the hooklets operate to maintain the vane structure. The barbules along one side of the barb carry hooklets and overlap and become attached to a row of node-carrying barbules of the adjacent barb.

Figure 9a shows two vane barbs side by side and clearly shows how the hooklets operate. Figure 9b is a drawing made by Robert Hook in 1665 which shows surprising similarity to our modern day photograph.

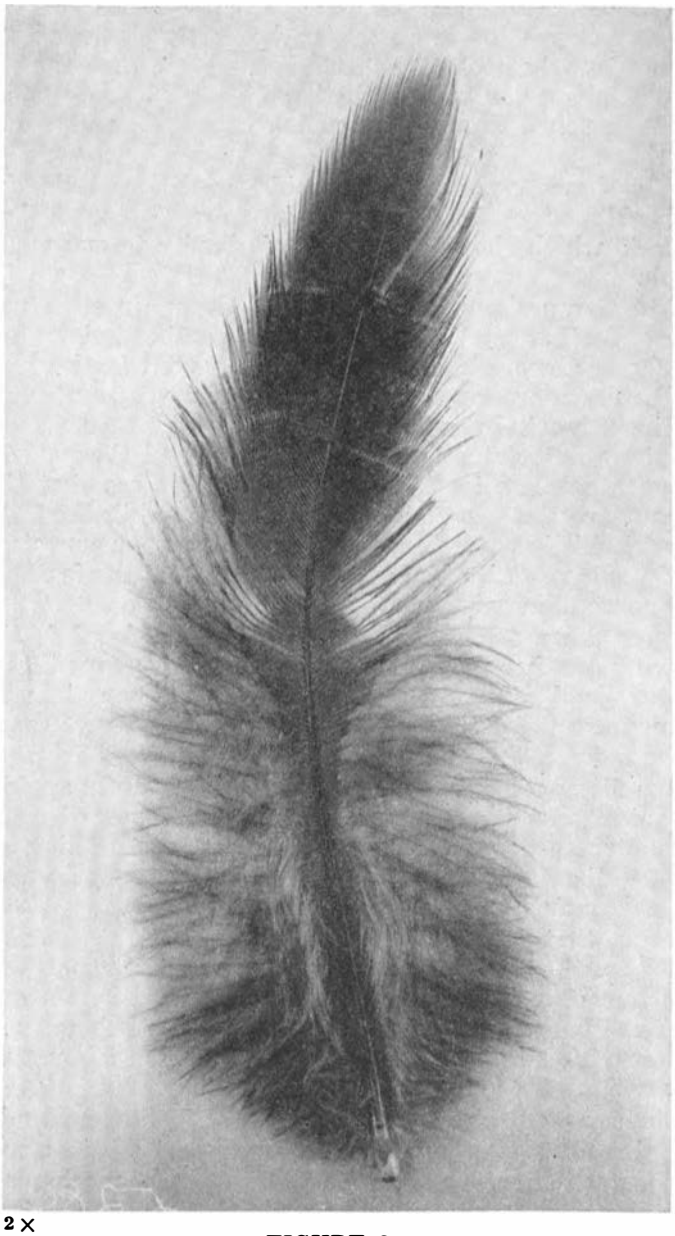
Figure 10 shows simplified sketches of the main structural characteristics of feathers and down. Front, side and end views are shown for a cluster of down, a fluff feather and a vaned feather. All three views of the down are two-dimensional showing the entire cluster to be three-dimensional. In contrast to this is the fluff feather whose end and side views are virtually one-dimensional and the vaned feather which is even more so in this respect. Thus we see that the vaned feather is a nearly flat two-dimensional structure while the fluff feather approximates this in varying degrees depending upon curvature of the rachis and fluffiness of the barbs. It is evident that the feathers would have poor space-filling characteristics.

If one goes down one step in the structural scale of feathers and down he will note that the same two-dimensional versus three-dimensional picture is obtained for feather barbs and down filaments. Figure 11 shows a series of views similar to those in Figure 10 except that in this case a down filament, a fluff barb and a vane barb are shown.

The down filament shows the fibrillae emerging at an angle of 75 to 90° in a spiral sequence around the axis. They describe an overall cylindrical structure which has considerable space-filling capacity. In contrast to the down filament both fluff and vane barbs are exactly like their parent feathers, essentially flat.

Thus we see that down is three-dimensional both at its gross structural level as well as at the level of its component filaments. Feathers are doubly negative in this sense. The parent feather is essentially planar or two-dimensional and the same is true of its component barbs. It is not surprising that feathers are much poorer fillers than down since they will tend to layer, one upon the next.

The structure of down is quite interesting from the standpoint of its functioning at various loadings. At very light loads its compression resistance is due to bending of filaments. This is the mechanism which comes into play during the conventional filling power determination. At heavier loads the down cluster collapses. Compression resistance now occurs through interaction of an almost infinite number of fibrillae, which have a much greater load-bearing capacity. These two types of compression resistance can account in part for the failure of the filling



2×

FIGURE 8a

Chicken feather.

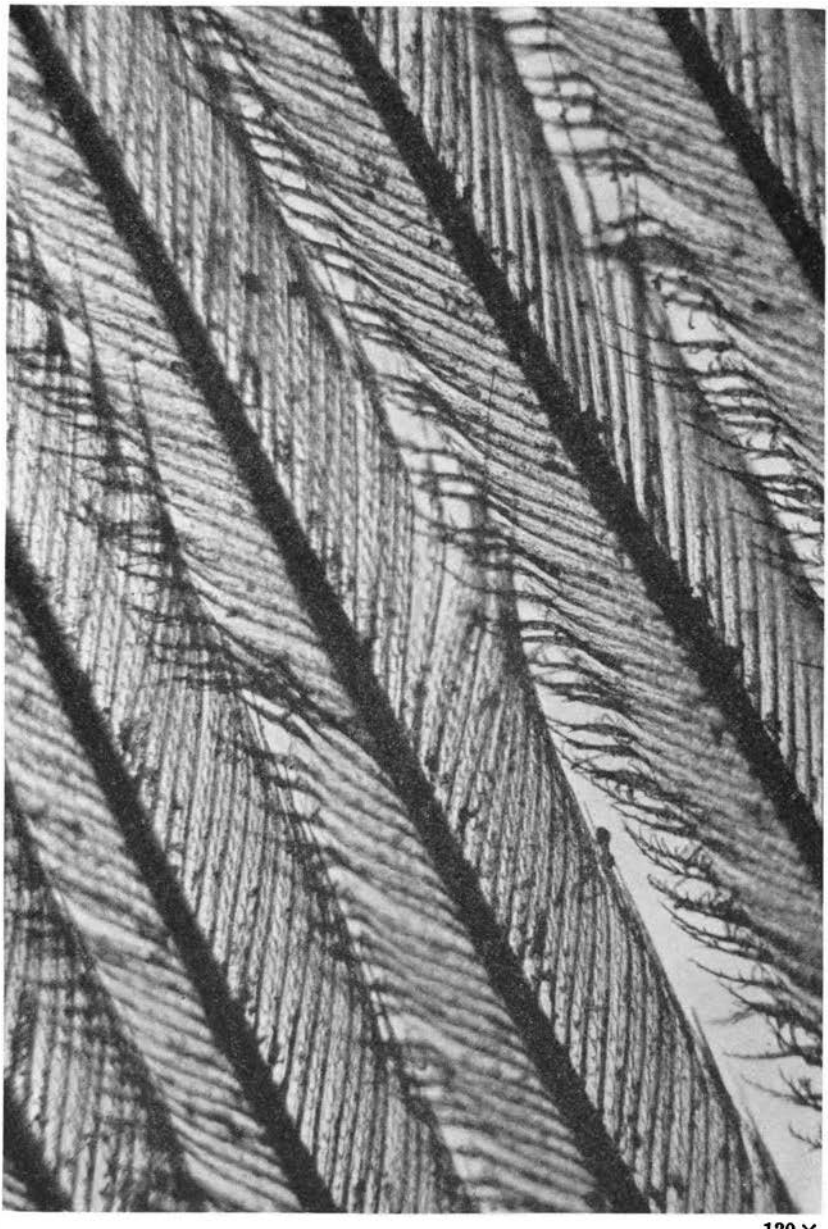
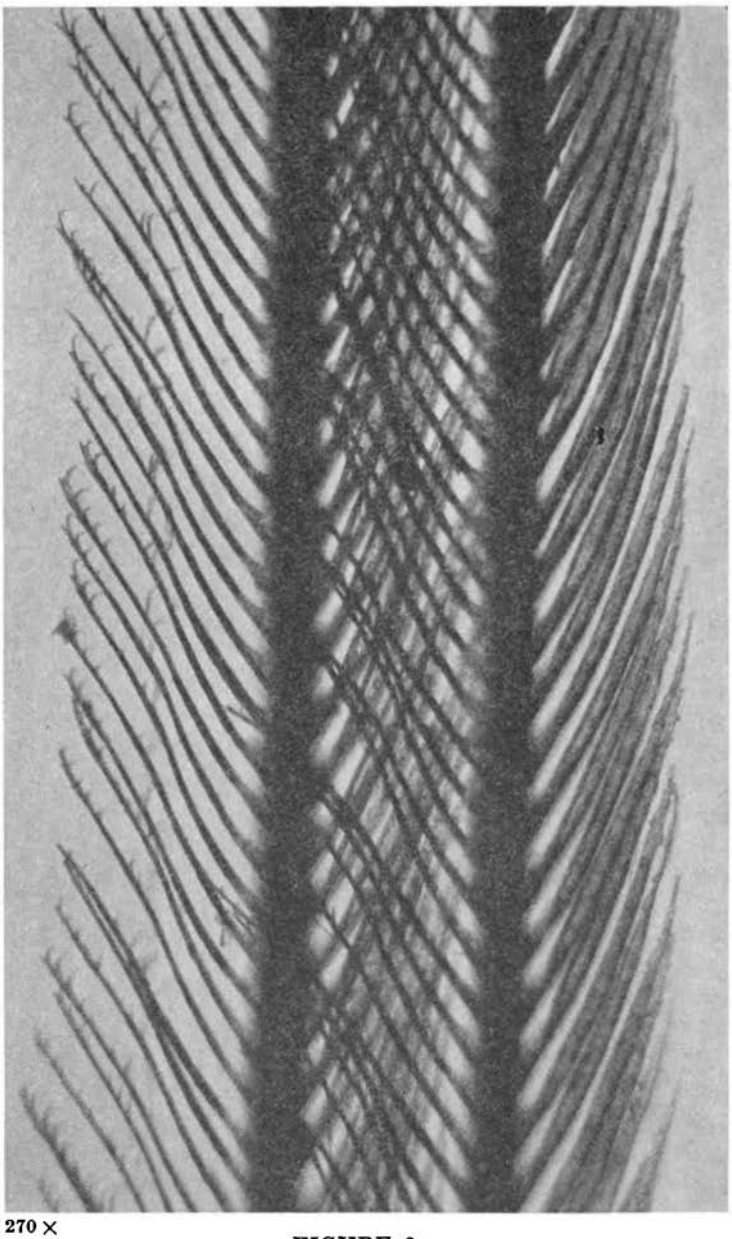


FIGURE 8b

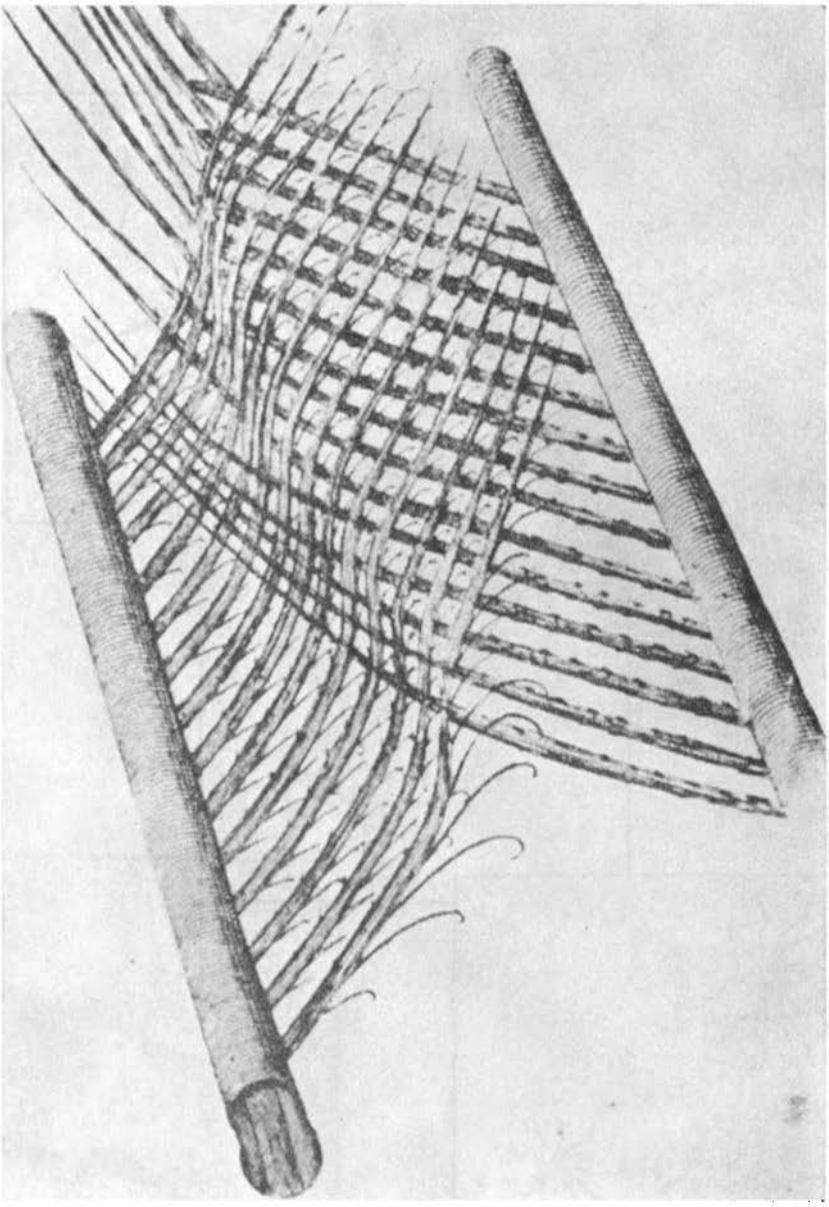
Vane barbs.



270 ×

FIGURE 9a

Vane barbs.



124 ×

FIGURE 9b

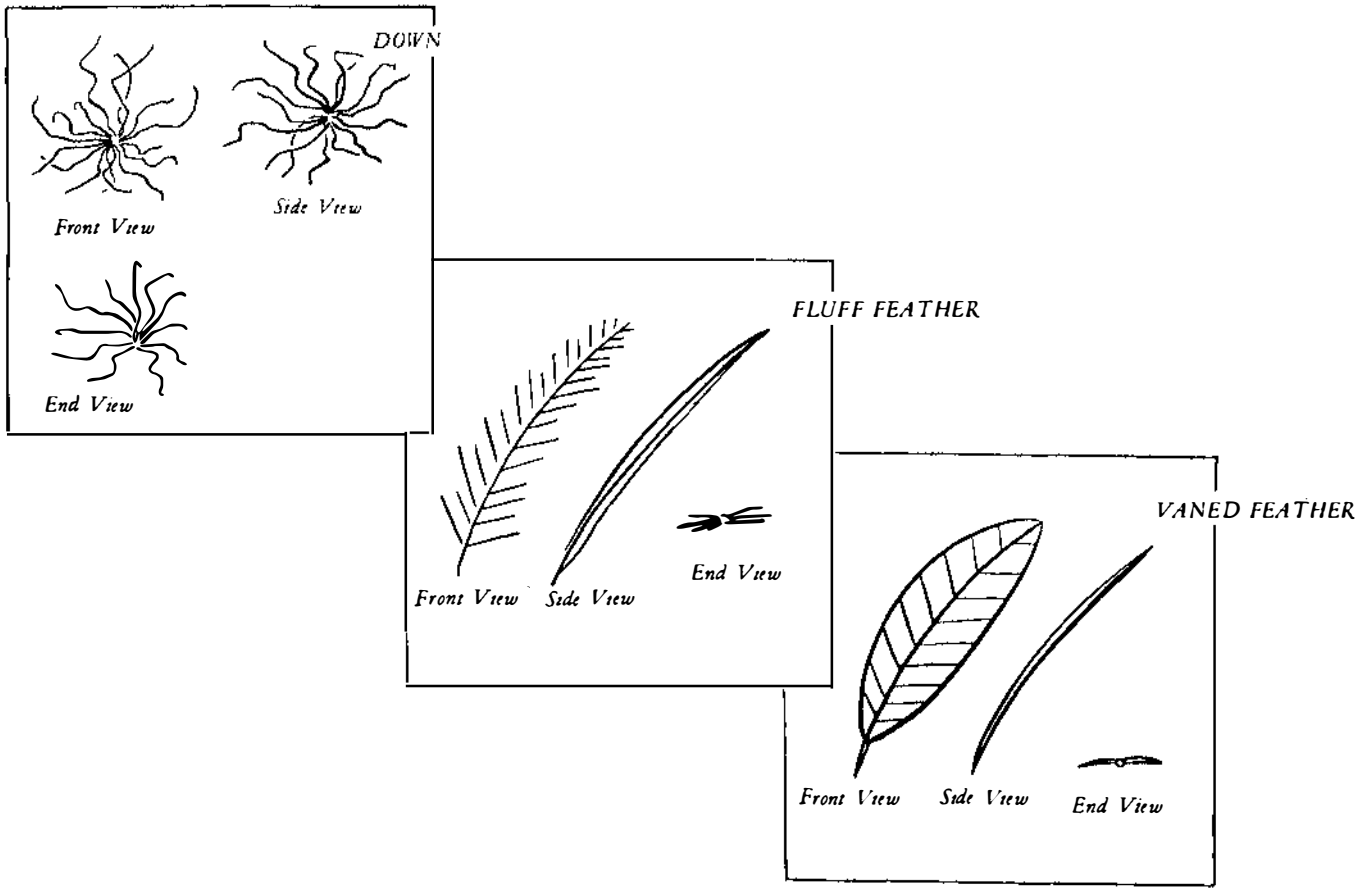


FIGURE 10

Schematic drawing of feather and down structures.

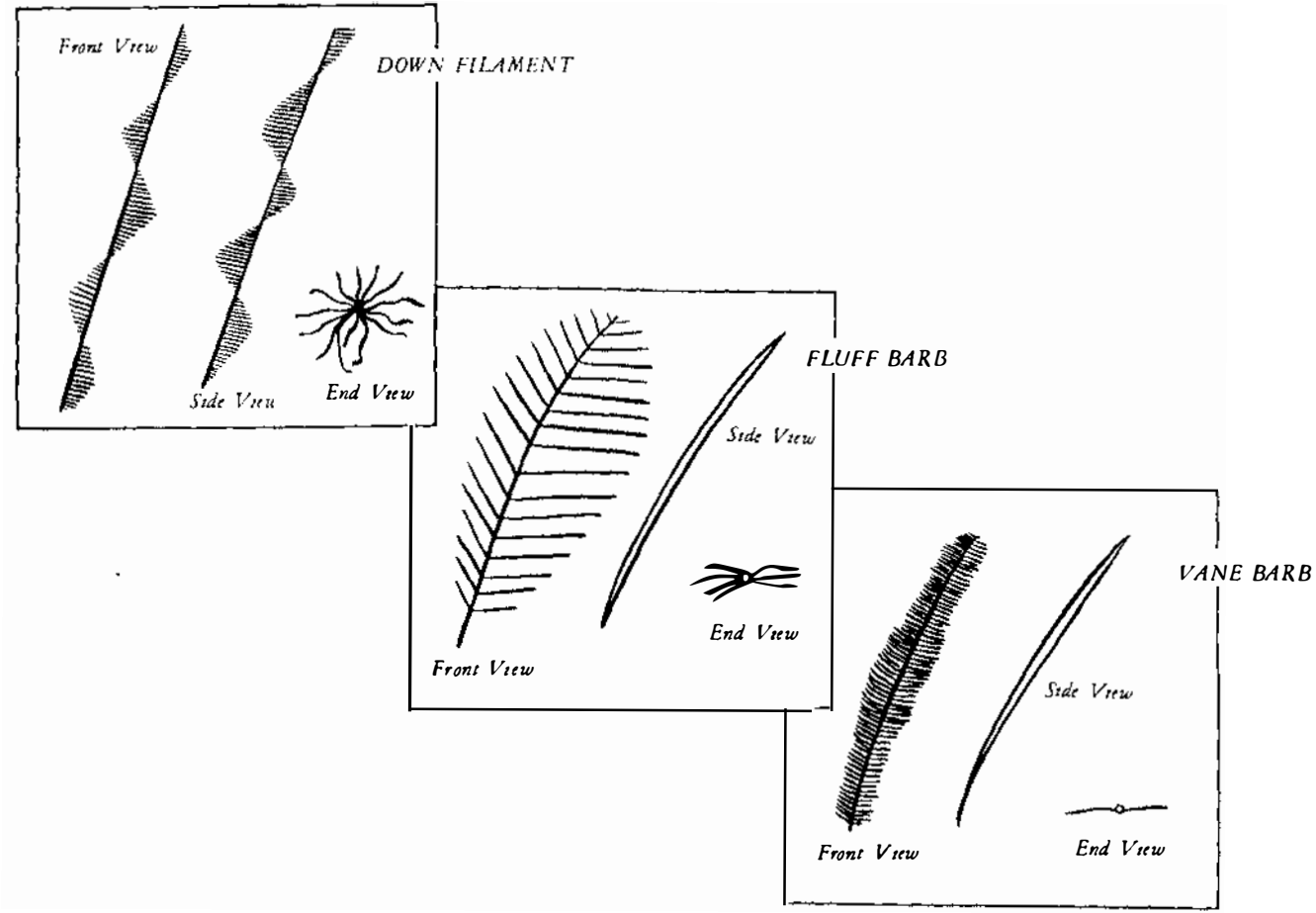


FIGURE 11

Schematic drawing of feather and down structures.

Goose down		
Filament	Length	20-31 mm
	Width	20-24 microns
Fibrilla	Length	.4-.7 mm
	Width	3.8-4.6 microns
Chicken feather		
Barb	Fluff length	37 mm
	Fluff width	15-140 microns
	Vane length	12-16 mm
	Vane width	5-70 microns
Barbule	Fluff length	.3-3.5 mm
	Fluff width	5-7 microns
	Vane length	.2-.5 mm
	Vane width	1-7 microns

FIGURE 12

power determination to accurately reflect the bulking qualities of a sleeping bag filler.

In addition to the major differences in morphology, there is a still further striking difference in fiber dimensions, total fiber length and number of individual fibers in equivalent weights of feathers and down. Figure 12 shows some length and width measurements for goose down and chicken feathers. The length of down filaments is intermediate between that of a vane barb and a fluff barb of a feather. There is a very substantial difference in widths, however. Down filaments have a quite uniform width of 20 to 24 microns but fluff barbs range between 15 and 140 microns while vane barbs have a range of 5 to 70 microns. It is believed that the much thicker basal portions of barbs contribute much to the weight of the filler and substantially less to the bulking capacity in comparison to down filaments.

Perhaps a more striking difference are the data in Figure 13 showing the number of individual fibers and the total length of fibers in equivalent weights of feathers and down. In a single gram of down

European goose down	
No. of clusters per gram	845
No. of filaments per gram	77,000
No. of fibrillae per gram	91,000,000
Total fiber length:	
Per cluster	65 yards
Per gram	31 miles
Per 4# sleeping bag	56,000 miles
Chicken fluff feathers	
No. of 89 mm feathers per gram	45
No. of barbs per gram	26,000
No. of barbules per gram	19,000,000
Total fiber length:	
Per feather	340 yards
Per gram	8.7 miles
Per 4# sleeping bag	16,000 miles

FIGURE 13

there are 77,000 filaments and 91,000,000 fibrillae which yield a total fiber length of 31 miles. In contrast to this a gram of chicken fluff feathers has 26,000 barbs and 19,000,000 barbules with a total length of 8.7 miles. The far greater number of fibers in down gives rise to an infinite degree of fiber-fiber interaction and consequently a higher bulking capacity. Since the total fiber lengths and number of fibers in down and feathers have a roughly comparable relationship as their filling powers it appears that these data have great significance.

Still another factor accounting for substantial differences between the bulking capacities of feathers vs. down is the amount of quill or body attachment present. It is apparent that feather quill contributes much to the total weight but since it is a heavy, compact structure, it has low space-filling characteristics. The same is true of the body attachment of down. Figure 14 shows the percentages of these por-

WEIGHT RATIOS OF QUILL OR BODY ATTACHMENTS

Feather	Percent quill
Rhode Island red vane	56
Green Pekin duck vane	43
New Hampshire red vane	38
European goose vane	31
Turkey 1-3 vane 2-3 fluff	26
New Hampshire red fluff	25
Rhode Island red fluff	23
Turkey fluff	18

Down	Percent body attachment
Green Pekin duck	23.6
European goose	12.3
North China duck	4.5
Eider	3.3

FIGURE 14

tions of the structure for different types of feathers and down. The vaned feathers have the highest amount of quill; the fluff feathers have less. This is in direct relation to their bulking values.

There is a surprisingly wide spread in the amount of body attachment in different downs, the eider and China duck downs showing very low values and the Pekin duck a very high value, in fact, higher than the amount of quill in some feathers.

Since the feather is essentially a planar structure, the rachis or quill is making two negative contributions to filling power. In the first place, it is maintaining the barbs in a planar orientation. Secondly, the rachis, being a high weight-low volume structure, is just so much dead weight. By removing the rachis as is done in the production of feather fibers we eliminate this excess weight and also permit the barbs to orient themselves in a random fashion.

We might note here that any attempt to increase the filling power

of feathers by crushing, curling, chemical treatments, etc., must consider the limiting factor of rachis weight. For example, if one were to attempt to improve the filling power of a feather whose rachis constituted 50 percent of its total weight, only half the feathers would be susceptible to improvement. If this filling power improvement is due to a substantial curvature of the rachis or to fluffing of barbs around the rachis, then its presence is necessary to maintain form. In this case, the rachis is not dead weight but is contributing a share. However, it will be important to determine the relative contributions to form and to weight in order to assess the net effect of the presence of the rachis.

I would like now to sum up briefly the main structural features of feathers and down which play an important role in filling power.

1. Down, at its gross structural level as well as the level of its component filaments, is three dimensional and therefore has good space-filling characteristics. Both the entire feather and its component barbs are basically two-dimensional and therefore tend to pack readily.

2. Down has a much greater number of individual fibers and total fiber length than feathers. These contribute greatly to the superiority of down.

3. Feathers have a very high percentage of "dead weight" rachis which contributes more to total weight than to bulking capacity.

CHAIRMAN SCHUBERT:

The next paper is entitled "Physical Properties of Feathers and Down with Particular Reference to Their Use as Filling Materials in Sleeping Bags." It is by Mr. Louis I. Weiner, who is the head of the Textile Engineering Laboratory, which is part of the Textile Clothing and Footwear Division of the Quartermaster Research and Development Command here at Natick headed by Dr. S. J. Kennedy.

PHYSICAL PROPERTIES OF FEATHERS AND DOWN WITH PARTICULAR REFERENCE TO THEIR USE AS FILLING MATERIALS IN SLEEPING BAGS

LOUIS I. WEINER

Textile Engineering Laboratory, Quartermaster Research and Development Command

During World War II the armed services for the first time faced the problem of conducting combat operations in the arctic and subarctic regions of the world. The need to protect troops against the hazards of the climate in these areas led to the development and widespread use of the present type of sleeping gear. The basic requirement of army sleeping gear is to provide enough warmth and comfort so that the soldier may obtain 6 hours of restful sleep every 24 hours in environmental conditions with temperatures ranging from plus 55° to minus 65° F. The design of the sleeping bag and the materials used

facilitate achieving this goal. For example, the form-fitting mummy-like shape of the bag immobilizes warm air around the occupant and the tight closures reduce the possibility of loss of the warm air. The use of water- and wind-resistant fabrics as encasing materials reduces the absorption of water and minimizes evaporative heat loss from the bag components. But most important is the filling material that is used, namely waterfowl feathers and down, whose inherent qualities make it ideal for sleeping gear.

The two major requirements of a filling material for sleeping bags are the maintenance of maximum bulk or volume when the item is in use, and conversely the achievement of minimum bulk or volume when the item is not in use. These apparently conflicting volume requirements have led to the somewhat facetious observation that the ideal filling material should have high compressibility in the daytime and

FIGURE 1

low compressibility at night. Of all the natural and synthetic products that have been studied and evaluated, feathers and down best meet these requirements. For example, as shown in Figure 1, a feather and down filled bag when fluffed for use has an approximate volume of 6 cubic feet, but when rolled by hand for carrying has a volume of ⅔ cubic foot.

Neither feathers and down, nor any filling material, can completely meet the requirements of high bulk for sleeping and low bulk for carrying. However, the requirements of bulk for sleeping are somewhat different for the bottom and for the top of the bag. In the bottom of the bag resistance to compressive pressures of the order of 3 lb/sq. in. would be required, while in the top of the bag pressures of less than $\frac{1}{100}$ of this are encountered. In the present concept of the sleeping bag, it is considered much more important to maintain bulk for insulation in the top of the bag. Only minimal insulation is required for the bottom of the bag since supplementary insulating materials may be placed under the bag, such as foliage, clothing, and inflatable pads.

Of all filling materials, feathers and down have the greatest bulk under the low pressures encountered in the top of the sleeping bag, and the least bulk under the high pressures applied in packing the bag to facilitate carrying.

While these requirements of high bulk and compressibility are of basic importance in sleeping bag design, they are not the only functional requirements that must be considered. The most important characteristics are listed in Table I.[1]

Because of this fact, investigations were made to find one measure or test that could be used to characterize the properties of a filling

TABLE I

FUNCTIONAL REQUIREMENTS OF FILLING MATERIALS FOR USE IN SLEEPING BAGS [a]

Filling power	Ability to maintain large volume under low pressure
Compressibility	Ability to be compressed to a small volume under high pressure
Resilience	Ability to return to original volume when compressive forces are released
Fluffability	Ability to redistribute filler to maximum volume in bag by mechanical agitation such as shaking
Low absorption	Ability to repel water
Softness	Free of irritating elements such as stiff quills
Drapeability	Ability to conform easily to the contours of the body
Warmth	This factor is related to many of those listed above
Cleanliness	Including freedom from odor, mildew and moth infestation
Fire resistance	Highly desirable
Launderability	Capable of being easily laundered without losing any of above properties
Durability	Ability to maintain optimum physical and mechanical properties after continued use

[a] Examination of this list will reveal that some of the physical and mechanical properties, including warmth, may be interrelated.

material of importance for use in sleeping bags. It must be recognized that no single measure can completely characterize materials as complex and variable in morphology as feathers and down. Nevertheless, studies made in several laboratories showed that the bulking value or "filling power" (which is the capacity of a unit weight of the material to fill a given volume at a low pressure) is a critical property of feathers and down and will more closely describe the functional suitability of these materials than any other physical or mechanical test procedure that has been developed.

Several methods have been investigated for measuring filling power.

[1] The definitions given for the terms in Table I are applicable only in the context in which they are used in this report.

One of these has been standardized and is used as a basis for the specification of all feathers, down, and feather products purchased by the Quartermaster Corps.[2] It will be useful to briefly review the significance of the filling power test and to show how, in the case of feathers and down, it is related to: (1) compressibility, which can be used as an index of the portability of sleeping gear; (2) resilience, which will indicate the ability of the feathers to recover from compressing deformation and (3) warmth, or the ability of the material to reduce heat loss from the body of the occupant of the sleeping bag.

A measure of the filling power, compressibility and resilience of feathers and down may be obtained by observing the change in volume or thickness of the material in a cylindrical container as the pressure is increased from a nominal load to a rather heavy load, and then returned to the original condition. The selection of the loads is of necessity rather arbitrary. However, for any given set of conditions the comparative filling power, compressibility,[3] and resilience of a group of materials may be computed as illustrated in Figure 2.

Measurements of filling power, resilience and compressibility made by the National Bureau of Standards and the Beltsville Laboratory of the Department of Agriculture have shown that there is a relationship among these parameters for feathers and down. The points on the graphs of Figure 3 were computed from data obtained by the National Bureau of Standards (11, pp. 68 and 139) on pillows filled with different types of feather materials. The original data have been normalized to a constant weight basis, so that the values given will be comparable. Examination of the curves indicates that both compressibility and resilience when expressed on an absolute and relative basis bear a linear relationship to filling power. The conclusion that may be drawn from this is that those feather products that have the highest filling power will also possess superior compressibility and resilience.

In Figure 4 data obtained at the Beltsville Laboratory (1) using a modified IP-2 inclined plane tester are plotted as effective compressibility and resilience[4] against filling power. Here again the linear

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[2] Specification MIL—F—5652C, 29 May 1953.

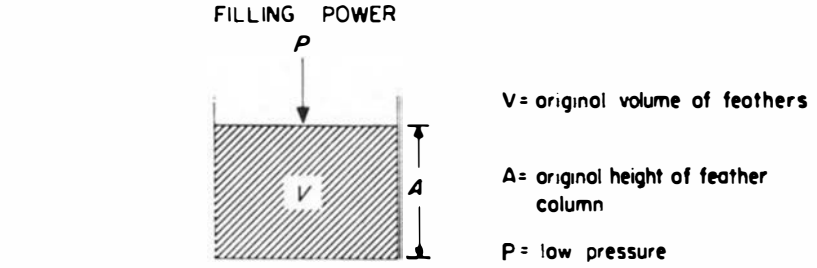
[3] Classically, compressibility is defined as the reciprocal of the bulk modulus (modulus of volume elasticity)

$$\frac{\frac{V_1 - V_2}{V_1}}{P_2 - P_1}$$

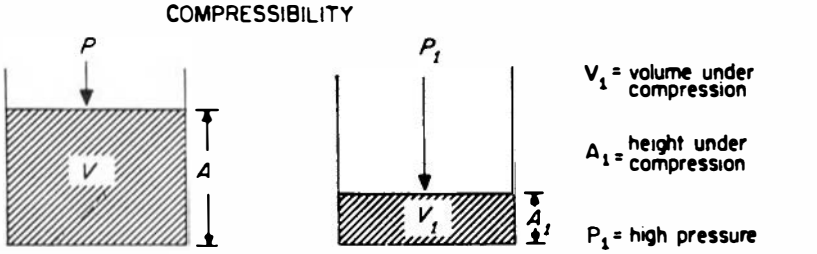
Where V = volume, P = pressure, subscripts 1 and 2 refer to the initial and final conditions respectively (Handbook of Chemistry and Physics, 33rd ed., Chemical Rubber Co., Cleveland, Ohio).

For the purpose of this paper compressibility and resilience are computed from noted volume or thickness changes only, ignoring the pressure required to produce these changes.

[4] Use of the term "effective" compressibility and resilience refers to the fact that measurements were made after three complete compression-relaxation cycles to remove most of the time-dependent stresses and strains in the sample. The pressures used in measurements were 100 g/in^2 and 10 g/in^2. Relative values shown in Figure 4 are computed on basis of recovered thickness, not original thickness.



Filling power may be expressed as the volume of feathers, V, or height, A, under low pressure, P It is usually expressed as A, the height of feathers in the column

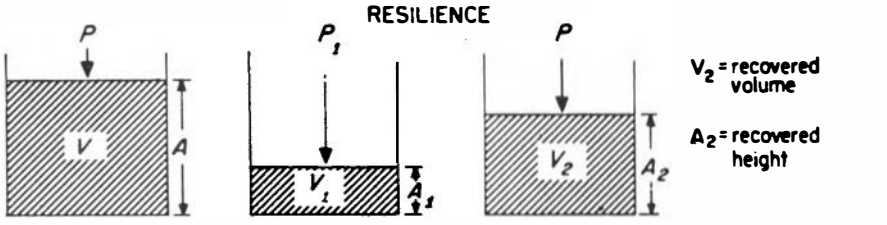


Compressibility may be expressed as the difference in volume or height of the feather column before and after compression

$$V - V_1 \quad \text{or} \quad A - A_1$$

It may also be expressed as a ratio to the original volume or height:

$$\frac{V - V_1}{V} \quad \text{or} \quad \frac{A - A_1}{A}$$



Resilience may be expressed as the difference between the recovered volume or height and the compressed volume or height:

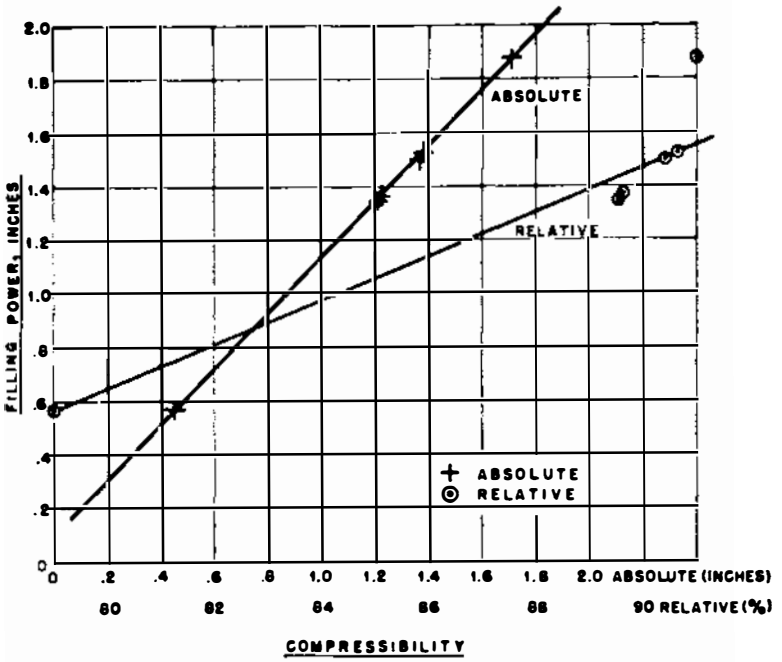
$$V_2 - V_1 \quad \text{or} \quad A_2 - A_1$$

It is usually shown as a ratio to the compressibility:

$$\frac{V_2 - V_1}{V - V_1} \quad \text{or} \quad \frac{A_2 - A_1}{A - A_1}$$

FIGURE 2

Pictorial representation of bulk parameters of filling materials.



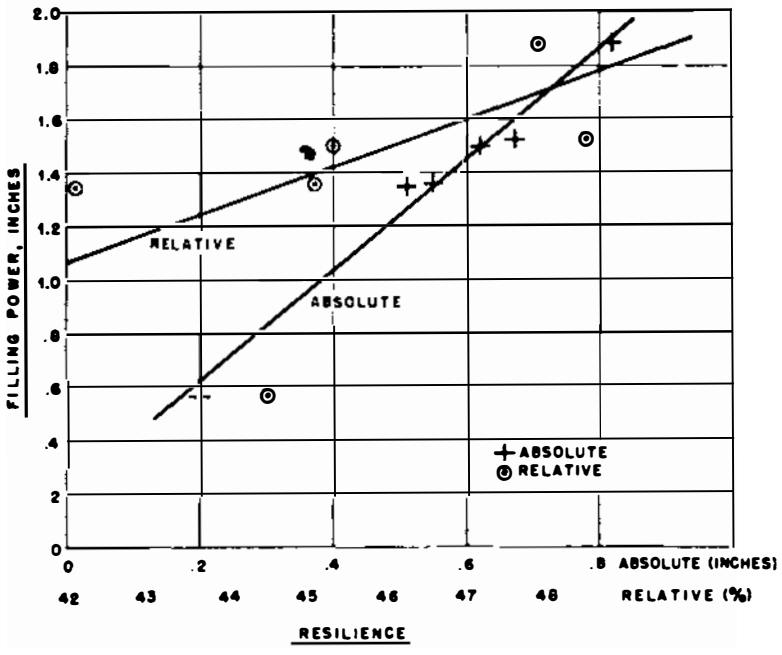


FIGURE 3

Relationship of compressibility and resilience of feathers to apparent filling powers as measured by the thickness of pillows under varying loads.

relationship is obvious. While it has not been possible to explain these relationships theoretically, the trends that have been observed are convenient in that the filling power measurement may be used as a means of assessing the useful mechanical properties of feathers and down.

Of equal significance from the standpoint of sleeping gear applications is the relationship of filling power to warmth, or more precisely to thermal insulation. The primary mechanisms for passage of heat through a sleeping bag, assuming that the insulation is dry, are by convection and conduction. Heat loss by convection will be appreciable unless the thickness of the free air spaces or cells can be reduced by the use of bulk elements such as feathers and down. The critical thick-

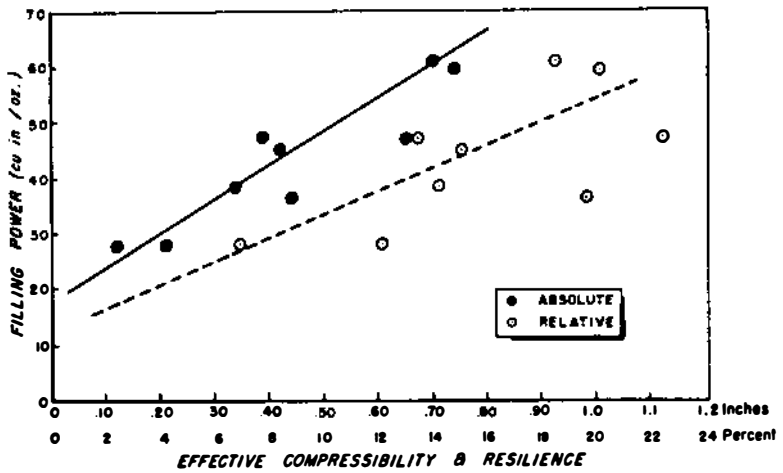


FIGURE 4

Relationship of effective compressibility and resilience to apparent filling power as measured on a modified IP-2 tensile tester.

ness of the air cells above which heat loss is accelerated has been stated by Siple (4) to be 0.5 inches. Others have given different values as low as 0.08 inches. Figure 5 illustrates the general shape of the thickness versus thermal insulation curves where convective and conductive mechanisms predominate (9, 10).

In the case of feather insulating materials, the approximate linearity of the thickness versus thermal insulation curve indicates that the prime method of heat transfer is by conduction or a combination of conduction and convection in which flow resistance for both heat and mass transfer is linear with thickness. A series of experiments in which the CLO[5] values of sleeping bags were obtained with the filler

[5] One CLO is the heat required to maintain in comfort a sitting-resting subject at 70° F., air movement 10 ft/min, and relative humidity not greater than 50%. It is equal to the thermal insulation of an average man's suit. 1 CLO unit = 0.18° C. per calorie per sq. meter per hr (8).

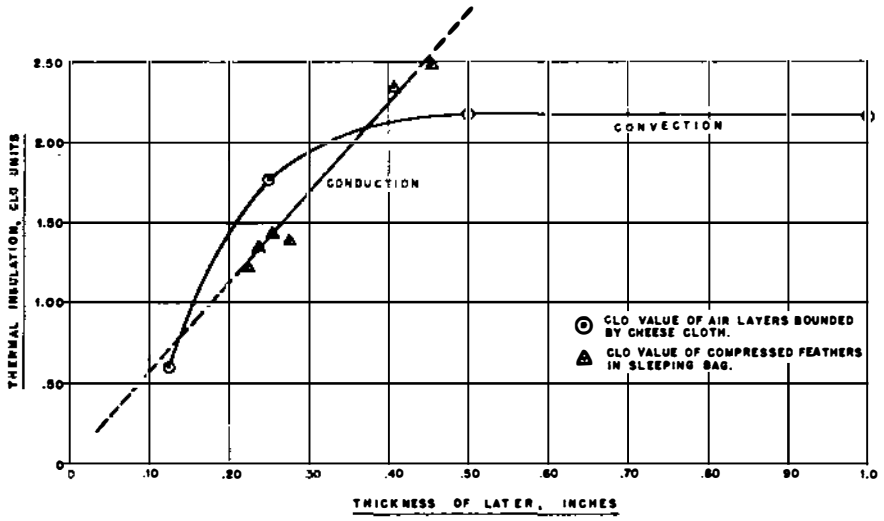


FIGURE 5

Relation of thermal insulation to thickness.

in a compressed as well as an uncompressed state illustrates this point. The data are plotted in Figure 6. Data for the thickness of the bag under compression were obtained by actual measurement (9).

Data for uncompressed thickness were derived from a standard curve showing the filling power of blends of feather materials (2).

One of the interesting properties of feathers and down is the pro-

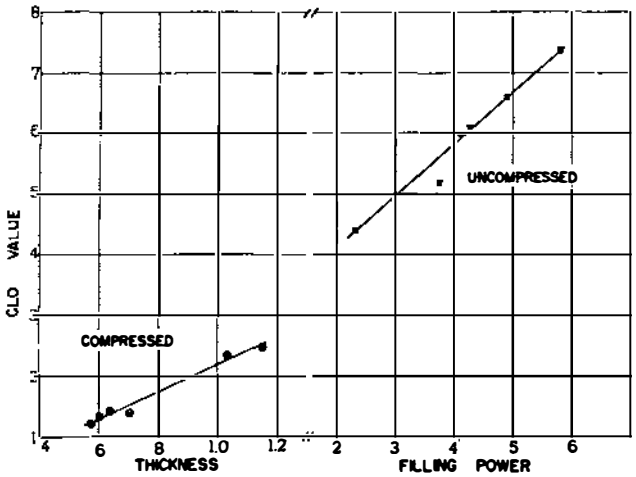


FIGURE 6

Relationship of old CLO value to thickness and filling power in compressed and uncompressed sections of sleeping bags.

portionality between filling power and sample weight. Thus, for a material "x" with a filling power of "x" cm. the relationship between filling power and weight may be illustrated as shown in Figure 7. For another material "y" with a filling power of "y" cm. a complementary curve may be drawn. To obtain the filling power of 0.9 of an ounce,[6] for example, of any mixture of "x" and "y", the individual filling powers must be multiplied by the fraction in which they are present and then totaled. If this computation is performed for the mixture of all weights that total 0.8 of an ounce, the filling powers of the combinations will be found to lie on a straight line drawn from "y" to "x" (7).

It is interesting to note that a deviation from this rule occurs at low concentrations of down in down-feather mixtures. This deviation might be considered to be an antisynergistic effect due to the fact that

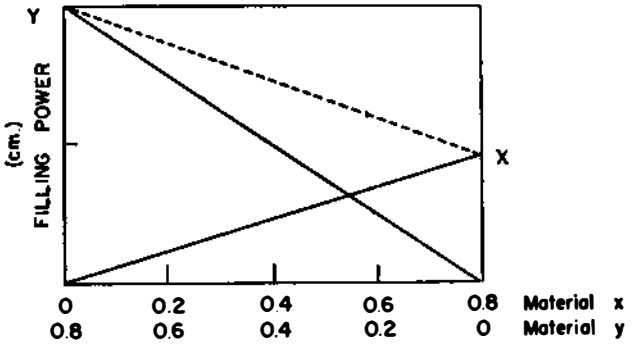


FIGURE 7

Relationship between filling power and weight of mixtures of filling materials.

the down will merely fill air space between the curled feathers without contributing to an increase in filling power. In fact, theoretically, the addition of a certain amount of down to feathers might actually decrease the filling power since down, while not contributing to the bulk, nevertheless preempts a part of the total weight. This observation suggests the possibility of obtaining greater value from sleeping gear by keeping the down and feather components in separate channels to prevent mixture. It has been estimated that under such conditions 28% down might provide as much bulk when used with 72% feathers as is currently provided by our standard 40% down, 60% feather mixture (6).

The importance of the study of the influence of feather mixtures on filling power is shown in the papers by Drs. Florio[7] and Frederick[8] which present details on the improvement in filling power achieved by

[6] The weight used in the standard filling power test.
[7] Of Alexander Smith, Inc., Yonkers, New York.
[8] Of Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania.

chemical modification treatments. Figure 8[9] shows how the filling power of a standard 40/60 down-feather mixture changes as the percentage of diluent is increased (2). It should be noted that dilution with untreated chicken feathers causes the greatest drop in filling power, followed by chicken feather fibers (which represent a finely divided feather substance obtained by mechanically separating the barbs and barbules from the quill and rachis elements). The slope of the acid-alum curve is quite gradual and it can be seen that as much

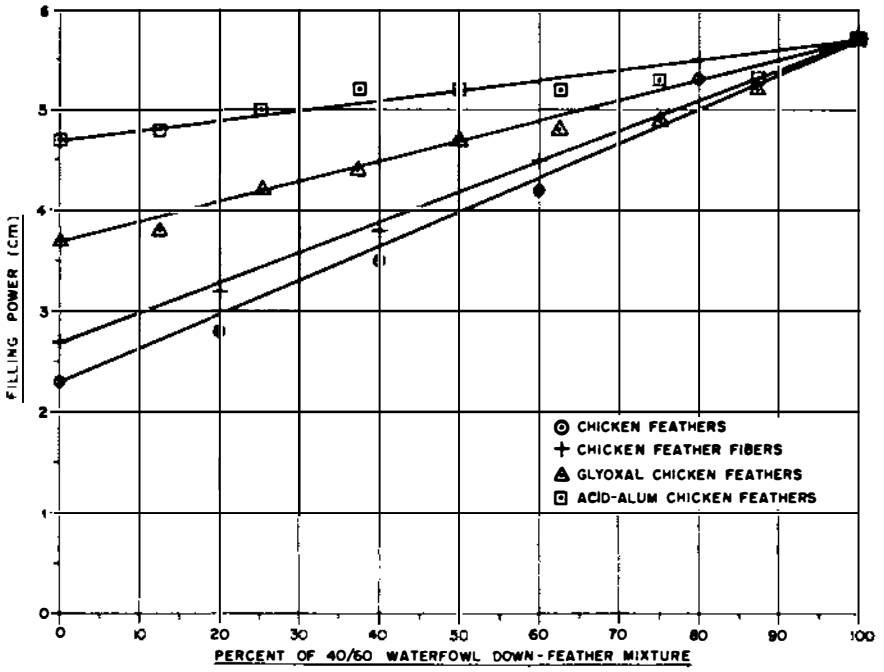


FIGURE 8

Filling power of mixtures of 40/60 waterfowl down-feathers with treated and untreated chicken feathers.

as 25% of these modified chicken feathers can be added to a standard 40/60 mixture without an appreciable loss in filling power.

Another factor that must be taken into consideration in comparing the relative value of modified chicken feathers with the natural product is the great variability that is inherent in the performance of different feather materials obtained from various geographic areas. For many years the Quartermaster Corps purchased feathers and down solely on the basis of geographic origin. While there is some

[9] Points on the graph represent the average of three experimental determinations, with the exception of the point at 100% 40/60 mixture, which represents the average of twelve measurements.

validity to this procedure, no definite rules can be made because of the variation in product from one source. In general, domestic and European materials are superior to those of Asiatic origin. However, individual samples have been analyzed in which this trend is reversed. The filling power test has eliminated much of the guesswork formerly used for determining the quality of feathers and down and makes it possible to discriminate between materials of different space-filling capacities regardless of their origin. Figure 9 presents the range in filling power of a variety of samples of down and waterfowl feathers obtained from seven geographic origins (11, p. 123).

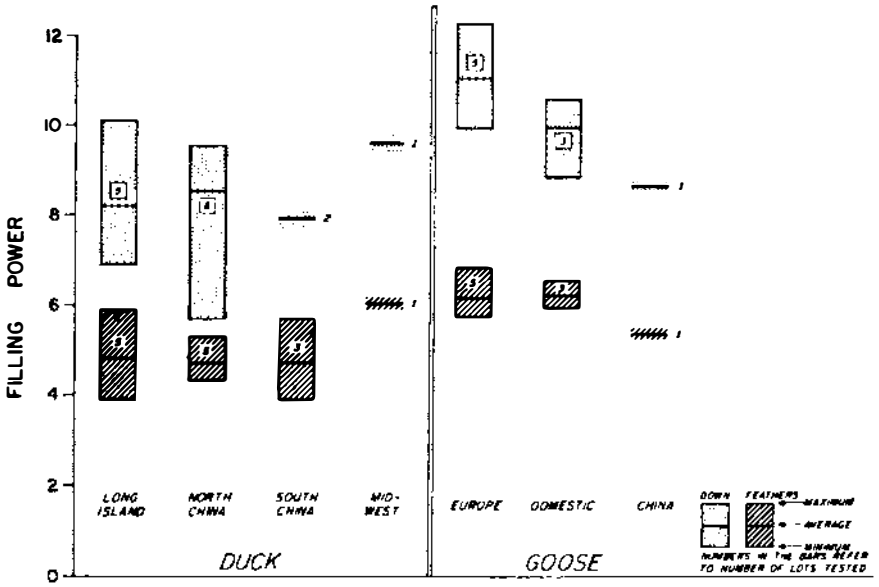


FIGURE 9

Range of filling power values of lots of down and feathers obtained from various geographic origins.

Measurements of the filling power of relaxed samples of feathers and down under different ambient conditions give variable results which may be explained in terms of the moisture relationships of the materials being tested. An increase in relative humidity will significantly increase the moisture content of the sample. While the added moisture increases the weight of the feathers, it makes no similar contribution to bulk and as a result the filling power of the sample will decrease. The change in filling power[10] that may be expected in down at different relative humidities is plotted in Figure 10. The curve has been plotted on the assumption that the normal value of the filling

[10] Filling power change was calculated from the change in weight due to moisture, assuming a linear correlation between weight and filling power.

power of down is obtained at 65% relative humidity which is the standard humidity condition for testing textile materials (5).

An appreciable increase in the apparent filling power of feathers and down may be caused by electrostatic charges developed during the fluffing of the material preparatory to the measurement of the filling power. Work done at the National Bureau of Standards has shown that it is possible to create an artificial charge in feathers and down by applying a direct voltage ranging up to 30 kilovolts to ioniz-

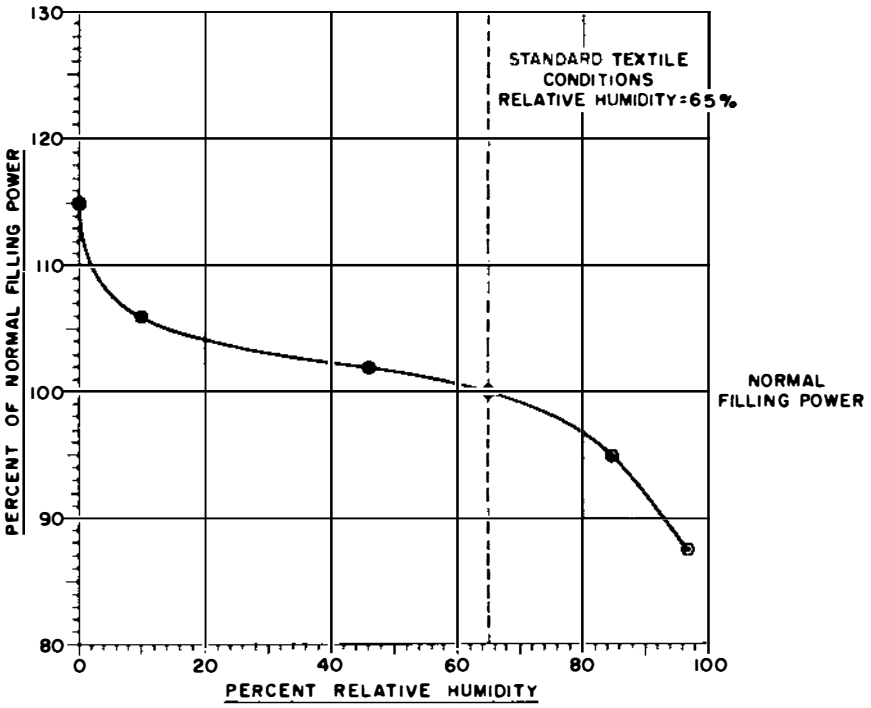


FIGURE 10

The effect of moisture content of goose down on filling power, assuming a relative humidity of 65% as standard.

ing points mounted above the container relative to a plate on the bottom (3). These electrostatic charges, generated either naturally or artificially, may be observed by measuring the potential of a small insulated metal probe inserted into the center of the charged material.

The error in filling power of a representative material expressed as the change in filling power from that at no charge is plotted in Figure 11 as a function of probe potential in kilovolts. It is obvious that the error for artificially developed charges is appreciable. One method of reducing the error due to the development of electrostatic charges is to allow a time lapse, during which the charges can recom-

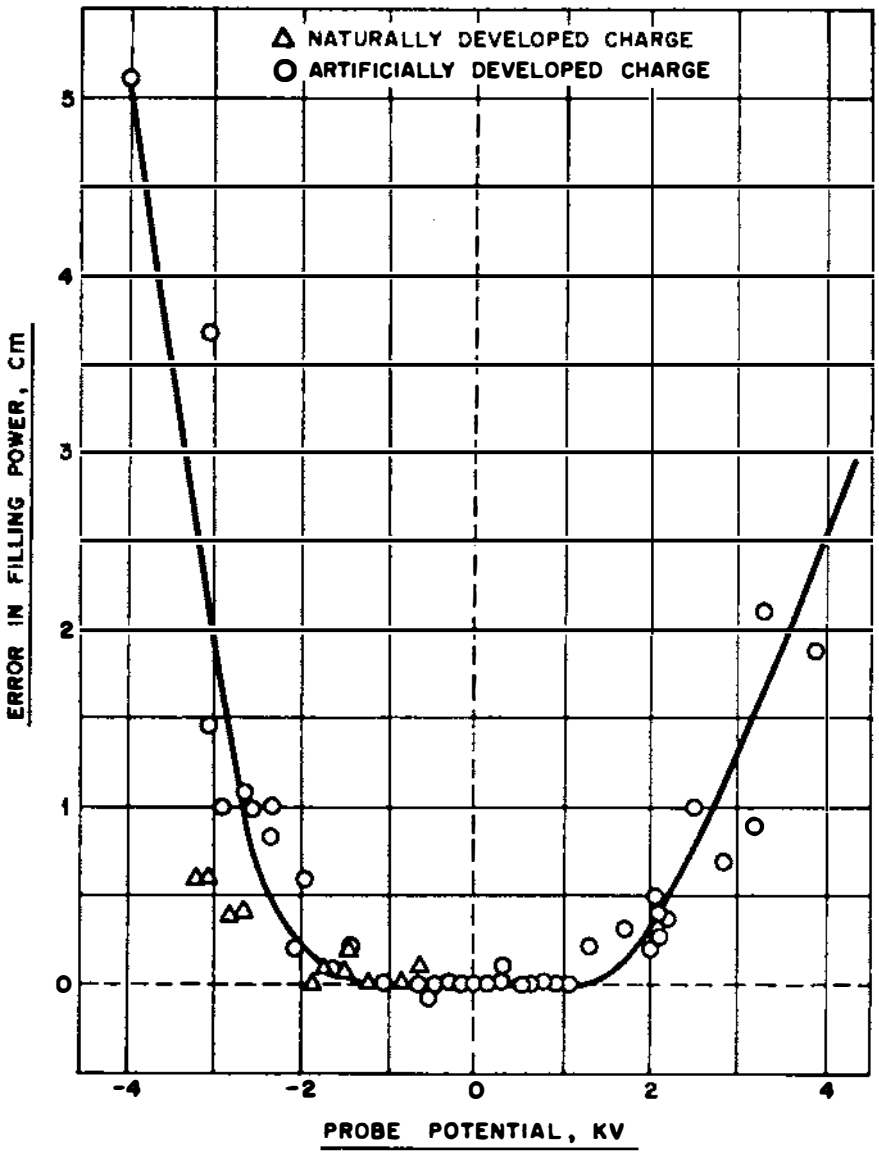


FIGURE 11

Relationship between probe potential and error in measured filling power of waterfowl down, due to natural and artificially generated electrostatic charges.

bine, before measuring filling power. Figure 12 shows the reduction of filling power with time decay of an artificially developed charge. From the curve it can be seen that a marked decrease in filling power error can be expected by waiting about 10 minutes for the charges to recombine (3).

In a short review such as this, it is not possible to describe completely all of the properties of feathers and down that must be considered for sleeping bag applications. Some of the properties that have been only mentioned (such as launderability and durability) may be of critical importance in eliminating the use of many materials which might have

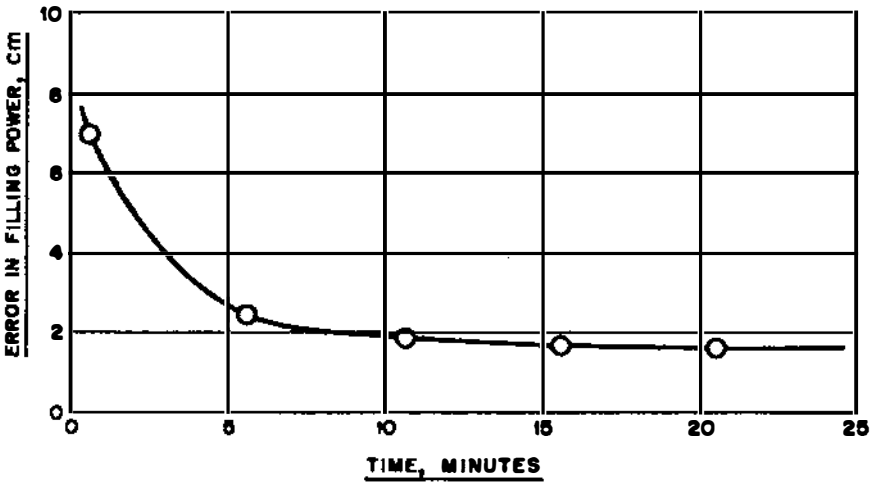


FIGURE 12

Error in measured filling power as a function of time elapsed after artificial charging of treated chicken feathers.

appeared completely satisfactory from an examination of the initial properties.

Probably the most significant data we have which point to the superiority of waterfowl feathers and down as fillers for sleeping gear arise from the unqualified endorsement given the sleeping bags by the men who must use them in the field.

There is no doubt that the very survival of the infantry soldier under the conditions of sub-arctic and arctic warfare depends upon our ability to provide him with suitable feather and down filled bags. The efforts of all of the technical personnel who have worked in this field, will have been well spent if the results contribute even in small measure to the comfort and efficiency of the combat infantryman.

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CHAIRMAN SCHUBERT:

Our next paper is on "Theoretical Considerations in the Chemical Modification of Chicken Feather Keratin." It will be presented by Dr. Robert M. Lollar. Dr. Lollar is Associate Professor in the Department of Applied Science in Tanning Research at the Institute of Scientific Research of the University of Cincinnati. Dr. Lollar has been with this department for more than eighteen years and is conducting some long range fundamental projects there including some for the QM Department.

THEORETICAL CONSIDERATIONS IN THE CHEMICAL MODIFICATION OF CHICKEN FEATHER KERATIN

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University of Cincinnati

The chemical modification of chicken feathers to improve their value as a filling material makes application of at least two fundamental properties of the chicken feather keratinous proteins. The first of these properties is the ability of these proteins to be swollen. This results in a distorted three-dimensional array of the barbs and rachis of the feather, so that the chicken feathers acquire a three-dimensional form comparable to that of waterfowl feathers. Hence, this results in a greater bulking value, as estimated by the filling power determination, with better insulating value. However, this modification of the feathers will not be permanent, especially during repeated washing of the feathers, unless advantage is taken of the ability to tan the proteins of the feathers, to fix this three-dimensional form.

An adequate understanding of the role of these two properties of the feather keratins requires some knowledge of the functional chemistry of the feather keratin. This information is presently available in a partial form only, but some suggestions from it to guide studies of the chemical modification would seem in order. Finally, some studies utilizing these ideas will be reported.

Recent reviews of Tristram (28) and Ward and Lundgren (30) have compared the composition of several keratins to one another. Table I gives analyses of chicken feather keratin in comparison to hair and wool. This table primarily utilizes original data secured by Graham, Waitkoff and Hier (10), Block (2), and Ward, Binkley and Snell (3), and includes data secured in the last decade.

The data in Table I for chicken feathers represent analyses on whole feathers. However, Lillie, in a review published in 1942 (16), emphasizes the independent origin of the central portion of the feather rachis and the feather barbs. The central portion of the rachis is derived from the central portion of a collar surrounding the feather papilla, while the barbs are formed from a special configuration next to the collar and near to the midventral line of the feather cylinder, which configuration is known as the ventral triangle. The base of the barbs, called barb petioles, conform to the shape of the central shaft, and are laterally bound together by keratinous fibers arising in each petiole. It is possible to separate the central and lateral components of the rachis by softening the feather in 5 percent potassium hydroxide, so that the barb petioles can be detached from the central rachis and from each other. Also, Lillie reviews information on the origin of the after-feather and the pulp of the growing feather.

Further, Leblond has reviewed work showing histological structural differences observed between hair and feather (15). The keratogenous

zone of hair is found to lie deep within the follicle, so that the exterior hair is composed of a fairly inert keratin. In the feather, the living or pulpy area in the feather cylinder extends outside of the epidermis. Further, at least in down feathers, the cortical keratogenous zone lies much further along the length of feather shaft than does the cuticle keratinization zone.

TABLE I

COMPARATIVE AMINO ACID ANALYSES OF KERATIN VALUES GIVEN AS GRAMS PER 100 GRAMS OF PROTEIN. RANGE SUMMARIZED FROM RECENT LITERATURE. (Primary reference, Ward and Lundgren (30))

Analytical characteristics		Specific keratin		
General type of analyses	Specific analyses	Chicken feather hard beta	Hair hard alpha	Sheep wool hard alpha
Component	Total Nitrogen	15.0 -16.2	15.5 -16.6[a]	16.2-16.9
	Amide Nitrogen	1.09	1.17	1.1- 1.37
	Sulfur	2.3 - 2.9	5.0 - 5.24	3.0- 4.0
Non-polar hydrocarbon residues	Glycine	7.2 - 9.5	4.1	5.2- 6.5
	Alanine	2.0 - 5.4	2.8	3.4- 4.4
	Valine	8.3 - 8.8	5.5 - 5.9[a]	5.0- 5.9
	Leucine	7.4 - 8.0	6.4 - 8.3[a]	7.6- 8.1
	Isoleucine	5.3 - 6.0	4.7[a]- 4.8	3.1- 4.5
	Proline	8.8 -10.0	4.3 - 9.6[a]	5.3- 8.1
Acidic residues (free or amide)	Aspartic	5.8 - 7.5	3.9 - 8.0[a]	6.4- 7.3
	Glutamic	9.0 - 9.7	13.6 -17.9[a]	13.1-16.0
Aromatic residues	Phenylalanine	4.7 - 5.3	2.7[a]- 3.6	3.4- 4.0
	Tyrosine	2.0 - 2.2	2.2 - 3.5	4.0- 6.4
	Tryptophane	0.7 - 0.9	0.4 - 1.3	1.8- 2.1
Basic residues	Histidine	0.3 - 0.7	0.6 - 1.1[a]	0.7- 1.1
	Lysine	1.0 - 1.7	1.9[a]- 3.8[a]	2.8- 3.3
	Arginine	6.5 - 7.5	8.9 -10.8[a]	9.2-10.6
	Hydroxy-lysine	—	0	0.2
Hydroxy-containing residues	Serine	10.2 -14	7.6[a]-10.6	7.2- 9.5
	Threonine	4.4 - 4.8	6.3[a]- 8.5	6.6- 6.7
Sulfur-containing residues	Cystine/2	6.8 - 8.2	14.4[a]-18.0	11.0-13.7
	Methionine	0.4 - 0.5	0.5[a]- 1.0	0.5- 0.7
	Cysteine	0.4	0.5 - 0.8	0.4

[a] Indicates hair values on hog hair, others on human hair.

Finally, it should be remembered that feathers may show the heterogeneity of composition observed by Mercer for wool (19) and by Tritsch for hog hair (29). Mercer has shown that the distribution of disulfide bridges within the cortex of wool is bilaterally dissimilar, resulting in the formation of two cortical halves with large dissimilarities of chemical properties. Tritsch (29) finds that the medullae of hog hairs are devoid of cystine interpeptide bridges. It does not appear immediately evident where such dissimilarity might be expected in feathers, but certainly these differences in the simpler hair or wool

fiber should suggest them in the similar but morphologically complex feather.

Corey and Schroeder, realizing the heterogeneous histological origin of feather parts, have secured some preliminary data (3) which have been rearranged to form Table II. These data were secured from three white turkey feathers, taken from immature birds. After physical separation of the four selected parts, the keratins were hydrolyzed for 24 hours in 6N HCl; the hydrolyzates were then analyzed for their amino acid composition by the Moore and Stein (20) ion exchange and starch chromatographic methods. Each figure is the result of a single application of the procedure. Corey and Schroeder caution against the extension of these preliminary data to the general case. In addition to the limitations imposed by the particular limited sample analyzed, it is necessary to investigate amino acid loss due to either incomplete peptide hydrolysis and/or amino acid decomposition.

Considering the species differences involved, as well as the differences in analytical methods, it is remarkable that the agreement is as good as it is. If the data in Tables I and II are computed on the basis of the number of individual amino acid residues per fixed length of polypeptide chain, e.g., per 100 residues (30) or per 10^5 grams of protein (28), it is evident that:

(a) Almost one-half of the residues are hydrocarbon in character in the feather keratin.

(b) About one-tenth of the residues in feather keratin originate from the amino acid, proline.

(c) Acidic and basic amino acids, responsible for the zwitterionic properties of proteins, account for only one-fifth of the residues. Arginine is the only basic amino acid occurring in large amount. The acidic amino acid residues outnumber the basic amino acid residues, but a significant portion of the acidic amino acids seem to be present in native feather keratin as the acid amides, asparagine and glutamine.

(d) The hydroxy-containing amino acids serine and threonine comprise one-fifth of the amino acid residues.

(e) The calamus and the rachis are fairly similar in amino acid composition, but they differ to some extent from the pith and to a greater extent from the barbs. It would be premature to comment further on these preliminary results.

(f) Complete accountability for the entire composition of feather keratin has not yet been secured. The analyses for cystine in particular should be regarded with some caution. However, the sulfur content of feathers seems to be low, and all published analyses indicate that keratins from feathers are deficient in cystine in comparison to other hard keratins, and may not exceed more than one residue in twenty.

The X-ray diffraction studies reviewed by Bear and Hugo (1) attest to the dissimilarity of feather keratin and hair and wool keratins. Table I notes that the hair and wool keratins are of the alpha type, while feather keratin is of the beta type. Mammalian hard keratins

and soft keratins of all animals studied give X-ray diffraction diagrams classified as the alpha type; in contrast, the hard keratins of birds and reptiles, including feathers, quills, scales, beaks, etc., naturally have a structure giving the beta diffraction pattern. Bear and Hugo propose a preliminary model for the feather keratin fibrils which assumes that the fibril is composed of large, globular particles, whose net-like organization is consistent with many of the features observed at small and intermediate diffraction angles.

TABLE II

COMPARATIVE AMINO ACID ANALYSES OF FEATHER PARTS
(Data of Corey and Schroeder (3); values given as grams per 100 g. of protein-dry, ash-free protein basis)

Analytical characteristic		Specific feather part			
General type	Specific analysis	Barbs	Calamus	Pith	Rachis
Elemental	Nitrogen	16.45	17.40	17.03	16.81
	Ash	1.48	2.00	3.80	1.04
Non-polar amino acid residues	Valine	7.68	7.49	6.95	7.29
	Glycine	7.27	9.72	8.78	10.26
	Alanine	4.04	7.38	5.94	7.85
	Leucine	7.24	8.70	8.13	9.32
	Isoleucine	5.05	3.86	3.77	3.92
	Proline	10.50	10.98	10.87	10.97
Acidic residues	Aspartic acid	6.21	7.17	7.00	7.38
	Glutamic acid	9.15	8.92	8.35	9.21
Aromatic residues	Phenylalanine	4.90	5.44	5.52	5.97
	Tyrosine	2.46	3.78	3.63	3.10
	Tryptophane	—	—	—	—
Basic residues	Histidine	0.38	0.54	0.78	0.27
	Lysine	1.16	0.87	1.31	0.87
	Arginine	6.48	6.79	6.49	6.25
Hydroxy-containing residues	Serine	12.25	13.43	11.53	12.90
	Threonine	4.54	4.25	3.97	4.26
Sulfur-containing residues	Methionine	0.36	0.34	0.44	0.39
	Cystine	6.43	7.72	7.13	6.67
	Free ammonia	2.00	1.69	1.68	1.76
Total		98.1	109.1	102.3	108.5

It may be noted that Corey and Schroeder (3) indicate that the presence of one residue in ten from the cyclic amino acid, proline, makes it highly improbable that the peptide chain could assume any of the pleated sheat or simple helical structures suggested by Pauling and Corey (22). Regardless of the final structural model which may be adopted for feather keratins, it seems obvious that the structural organization of feather keratin and hair and wool keratin is dissimilar. Thus, we have physical confirmation of the dissimilarity of the different keratins, which was indicated by the amino acid analyses.

Lundgren (18) has concluded that the proteins appear to be stabilized through a combination of dissociable salt linkages, hydrogen bonds and disulfide bonds. Further, Jones and Mecham (14) have observed that feather keratins are consistently the most readily dispersible of the various keratins they studied. Detergents and hydrogen bond breaking agents were found to be able to disperse feather keratins readily in the presence of disulfide-bond splitting agents. Thus, Ward, High and Lundgren (32) dispersed 63 percent of white Leghorn chicken feathers by boiling 16 g. of feathers with 11 g. of a sodium alkyl ($C_{12}-C_{14}$) benzene sulfonate and 1 g. of sodium bisulfite per 100 ml. of water. Numbers average molecular weights of the keratin moiety of the complex was 34,000, and the similar weight average molecular weight was 40,000. Feathers also have a larger fraction of the keratin soluble in hot aqueous alcohol in the presence of a reducing agent. Ward and Lundgren (30) observe that such conditions yield a fraction, comprising 80 percent of the feathers, whose molecular weight by osmotic pressure methods is around 10,000. They further note that this approximate molecular weight ratio is rather characteristic of many solubilized feather keratins, and that feathers are more precisely degraded than wool to fragments which have a relatively small range in size. It should also be noted that Jones and Mecham (14) found that disulfide reacting agents alone at a pH of 12.7 can disperse feather keratins.

It seems therefore evident that feather keratins are more susceptible to keratolytic agents than are the other keratins. It is important at this point to recall Lillie's observation (16) of the independent origin of the feather barbs and the feather rachis, and their separation in 5 percent KOH. All of these observations indicate that feather keratins must be much more carefully handled in contact with keratolytic agents than keratins like hair and wool. Thus, the use of conventional tannery unhairing accelerations to prepare feathers for subsequent treatment may seriously damage the feathers. In this regard, it may be recalled that Frederick (8) used 5 percent NaSH to prepare a feather fiber from feathers. The important point about this sensitivity of feather keratins to keratolytic or keratin-solubilizing agents is that it may produce a change in the characteristics of the feathers which the filling power test will be unable to detect. If the accelerator has merely weakened the attachment of the barb petiole to the rachis, or embrittled the barb, the static filling power test might fail to detect the change. It seems imperative to secure data on the effect of chemical modification of the keratins on the barb fragility and the feather resiliency.

Further, it is noted that the composition of the feather keratin imposes a specific reactivity on the keratin. The fact that half of the residues are hydrocarbon residues reduces the available reaction sites to only one out of two residues. Further, the low content of the basic amino acids and the presence of arginine as the only basic acid present

in large amount would imply that aqueous fixation of formaldehyde would be significant only at pH levels above pH 8. Hegman (12) has found this to be the case for duck feathers. On the other hand, Fraenkel-Conrat, Cooper and Olcott (7) criticize Hegman's use of bisulfite to remove unbound HCHO; further, at pH levels of 3.5 to 4 at 70° C., in the presence of 3.75 percent HCHO for four days, they find feather keratin to bind 8 moles of HCHO per 10^4 gram, while wool keratin bound 11 moles. For feather keratin, they attribute 60 percent of the HCHO binding to the acid amide groups, while with wool this amide binding is less than half of the total. Their conclusions on many proteins attributes the HCHO binding to a combination of the basic and the primary amide groups of the proteins. Their results would indicate therefore that an adequate aldehyde reaction with feathers would require retention of the primary amide groups as well as the basic groups.

On the other hand, the mechanism of mineral tannages normally assumes that the presence of the free carboxyl group is a requisite for mineral tannage (26). Thus, it is obvious that dissimilar preparatory conditions may be desirable to condition the feather protein for each tannage reaction.

It has been noted that the content of amino acids causing the zwitterionic properties of the proteins contributes only one residue in five. However, evidence does not seem to be available on the isoelectric point of native chicken feather particle, nor on the influence of any of the possible modifications on a shift in the isoelectric point. The excess of the acidic residues over the basic residues is complicated by the presence of the non-ionizing amide groups in the native protein. It therefore seems probable that treatment of the feathers with acidic or basic hydrolytic agents should make the isoelectric point of the feather keratin more acidic than that of the native keratin. In the case of collagen the isoelectric point shift is about 3 pH units, from pH 7-7.7 to about pH 4.8-5.0.

One-fifth of all of the amino acid residues in feather keratin arise from the hydroxy-bearing amino acids, serine and threonine; on the basis of the non-hydrocarbon residues, 40 percent of the reactive residues arise from these hydroxy-bearing acids. Lundgren (18) notes the binding of simple alcohols by feather keratins and feels that hydrogen bonding reactions between the peptide links as well as hydroxy-amino acid residues are involved. French and Edsall (9) note that formaldehyde and serine and threonine seem to react to form unstable oxazolidines. Further, it may be noted that extensive commercial use is made of glyoxal in the stabilization of such polyalcohols as cellulose and starch involving the curing of the glyoxal-polyalcohol in the presence of an acidic catalyst. Dihydric alcohols, in the presence of acidic catalysts, react to form cyclic acetals with the elimination of water. Hence, it seems possible that feather keratins may react with glyoxal as an alcohol. It is noted that the conditions of feather modi-

fication used in the Mellon process with glyoxal (8) include the acid catalytic conditions employed in the crease-proofing of cellulose (23).

The primary performance characteristic of a treated chicken feather is of course its value as an insulating filler in a sleeping bag. It is therefore logical to assume that the material showing the greatest bulking ability would have the greatest value as a sleeping bag filler. Entrapped air is an excellent heat insulator; hence, a high bulk feather product, capable of entrapping a large volume of air, should give a high insulating value for a small weight. Further, this large bulk is also capable of significant reduction at moderate pressures to permit pack transfer of the bags, yet the resiliency of the feathers permits ready re-bulking.

It is generally agreed that the Sinski filling power test (27) represents a practical method for the primary characterization of treated chicken feathers for use in sleeping bags. This method was developed from Edelman's "box method" (5, 24). Edelman found that very low loads applied to the feathers gave volume readings which were most sensitive to differences in feather, yet reasonable precision was retained. At zero load, the sensitivity was increased, but the precision was very low. At loads of 0.02 lb. per sq. inch, the sensitivity to detect difference was reduced at least 50 percent, with but little increase in precision. Hence, it was decided to use a load of 0.002 lb. per sq. inch in specifications employing the filling power test.

It should be realized that the selection of this load level was based upon considerations of precision and sensitivity of the laboratory measurement of the filling power, per se. However, Edelman (5, 24) observed that pressures between a person in a sleeping bag and the supporting surface exceeded 0.2 lb. per sq. inch. Further, Frederick (8) reports that subjects in sleeping bags in outdoor cold exposure tests experienced cold at the body pressure points, even though an inflated rubber pad or an additional sleeping bag was placed beneath the subject. Finally, Loconti and Bailey (17) have observed that at 0.002 lb. per sq. inch the bottom portion of the filling material does not support any of the weight of the filling power piston.

These observations have been recorded to illustrate that the actual use conditions imposed greater mechanical stresses upon the feathers than is applied in the evaluatory filling power test. Therefore, it is certain that the service comparison of the value of modified chicken feathers must also consider the influence of the modification upon the fundamental mechanical properties of the feathers. If treated feathers showing the identical filling power values of waterfowl feathers do not also match the mechanical properties of the waterfowl feathers under the loading conditions of actual use, the improved filling power may be of little practical value. This is particularly significant when it is recalled that chemical modification of keratins to produce fibers have customarily been unable to equal the properties of the natural wool fiber. If the chemical treatments to increase the static filling

power of the feathers simultaneously weaken the attachment of the barbs to the rachis, or decrease the resiliency of the barbs and the rachis, the increased static filling power will be deceiving. Hence, it seems imperative to guide theoretical studies on the improvement of the insulating power of modified chicken feathers with more fundamental measurements than the static filling power, a bulk volume measurement under the instantaneous application of a very low load. Barb attachment fragility and rachis resiliency measurements can readily be made on the Instron tensile tester. Further, with considerably more effort, barb resiliency measurements are possible. Further, these measurements of resiliency could be measured under dynamic conditions to note the fatigue characteristics of the treated feathers in contrast to waterfowl feathers. It seems desirable to use such tests to complement the static filling power test in the research development of improved chicken feathers.

The field use of the treated feathers must inevitably expose them to adverse hydrolytic deterioration. Use of the sleeping bags will result in feather uptake of water, both from body moisture and from the environment. Further, the feathers will gradually become soiled from perspiration and from environmental filth. These conditions will promote the growth of microorganisms upon the feathers with resultant development of offensive odor and unsanitary conditions. Hence, it is contemplated that the field use of the treated feathers will involve the washing of the treated feathers in the sleeping bags.

The uptake of water by the feathers, the growth of microorganisms on the soiled feathers and the washing of the feathers will all exert a hydrolytic action on the feathers. It has been noted that feather keratin is a more labile protein than wool or hair keratins, and it is noted that both of the existing feather modification processes involve a tannage process in the treatment. The tannage would give increased initial resistance to hydrolytic deterioration of the feathers, but the exposure conditions just described are able to bring about detannage.

This is particularly significant when it is realized that tannages differ markedly in their stability characteristics. Hence, it seems necessary to develop some form of accelerated aging and tannage stability tests to guide the research development of improved chicken feather products. Tests involving exposure to microorganisms, using odor development and bacteriological examination of the test feathers as evaluatory techniques, are feasible. Further, for certain tannages at least, detannage studies are possible; tannages such as aldehyde tannages will not be so readily evaluated for tannage stability because of the absence of suitable analytical techniques.

It is therefore proposed that theoretical considerations of the chemical modification of the chicken feathers to produce improved sleeping bag filler should use feather mechanical-property measurements, microbiological stability tests and tannage stability tests to complement the static filling power test. This combination of testing will give an

answer which enables a better prediction of the service characteristics of the treated feathers than the use of the filling power test alone.

During the past few months four different types of chemical modification of the feather keratins have been carried out in this laboratory:

(a) Investigation of the influence of the pH conditions upon the modification of the filling power of chicken feathers during reaction with glyoxal.

(b) Modification of the functional group reactivity of chicken feather keratin to improve the filling power of the feathers, as well as to improve the microbiological resistance of the feathers.

(c) Application of available information on the stability of tannage to modify the tannage stability of the Alexander Smith "Keracurl" process for the modification of chicken feathers.

(d) Study of the influence of keratolytic agents used in tannery beamhouse operations on chicken feathers.

It has been previously noted that there is some disagreement in the literature about the proper conditions for the reaction of proteins with aldehydes to secure aldehyde fixation. Fixation of formaldehyde by lysine and arginine residues seems to be favored by alkaline reaction conditions in both collagen and keratin. However, we have noted that Fraenkel-Conrat, Cooper and Olcott (7) secure significant HCHO fixation at acid pH levels. Frederick's conditions (8) for the glyoxal modification of chicken feathers involves acid fixation conditions similar to those used in the modification of polyalcohols such as cellulose (23). Discussions at the National Research Council committee meeting concerned with substitutes for waterfowl feathers have raised questions about the sufficient reaction conditions for this process. Further, Frederick (8) notes that the limiting conditions for the process are not known. Hence, it was decided to secure data relative to the influence of pH and catalytic agents in the Mellon process.

The feathers used were secured immediately after plucking from a commercial poultry dealer. The birds being plucked were immature, 11 week old, White Rocks. The wet feathers were brought to the laboratory and dried the same day. Portions of the dried feathers were weighed out for the particular modifications of the glyoxal process to be studied. All batches of the dried feathers were given the dual washing procedure specified in the Mellon process. For the blood solubilization bath, the dried feathers were wet back and then washed for 10 minutes at 120° F. with 1 liter of a 0.06 percent solution of Haemo-sol per 40 grams of air dry feather. After draining off the blood solubilizing agent, one liter of 0.25 percent Igepal CO-630, a non-ionic detergent of the polyoxyethylated nonyl phenol type, was added at 120° F. for 20 minutes. The detergent was then drained from the feathers, which were then treated with the several modifications of the Mellon procedure.

The several different batches of modified feathers were prepared:

(a) The conventional Mellon process, involving the use of a tri-

sodium phosphate curl inducement bath, and alum-glyoxal fixation bath, tumble drying, and elevated temperature curing. All subsequent batches were modifications of this same basic procedure.

(b) The second batch eliminated a washing procedure between the curl inducement and the addition of the glyoxal, so that the reaction pH of the feathers added to acid-glyoxal bath remained alkaline. Further, the acidity of the commercial glyoxal was not modified by the addition of alum. Hence, the reaction conditions would be less acidic than those in the conventional Mellon process.

(c) Both the curl inducement swelling and the glyoxal reaction was secured at acid pH levels. Acetic acid at the 0.1 N level was used for swell inducement, giving a final bath pH of 2.9. The glyoxal dilution without alum addition was found to have a pH of 2.6, and was used without any pH adjustment. Hence, this batch was prepared with an acid curl inducement and glyoxal fixation bath.

(d) The fourth batch was identical to the third batch through the removal of the first glyoxal solution. Then, a second 1 percent glyoxal solution was added after adjustment of the solution pH to 8. Intermittent agitation and pH adjustment over about a 1 hour period kept the pH of the second glyoxal bath between pH 5 and 8. Hence, the second glyoxal fixation was secured from a bath which was approximately neutral.

(e) The fifth batch was identical to batches (c) and (d) except that tri-sodium phosphate was used to secure an alkaline pH condition for the second glyoxal treatment. Intermittent agitation and pH adjustment kept the bath pH between 7 and 9 during a 40 minute period.

(f) This batch involved a phosphate curl inducement bath and an alkaline glyoxal fixation bath. The initial pH of curl inducement bath was 11.8, and the spent bath had a pH of 11.2. The initial pH of the glyoxal tannage bath was 8.4 and the final pH of the bath was 7.6. Hence, the total procedure involved alkaline reactions, and therefore contrasts to batch (b) which was acidic in reaction throughout both baths, while batch (a) involved the alkaline curl inducement, but the acid glyoxal fixation reaction.

Table III presents results secured from this experimental series of batches. Discussion of the significance of the results will be found in a later section of the report.

It has been noted that the reactivity of the feather keratin for the several possible chemical methods of modifying the filling power of feathers should be related to the functional groups in the amino acid residues. Herriott (13) has reviewed the reactions of native proteins with chemical reagents. Further, Zahn et al. (33) have reported upon the preparation of microbiologically resistant wool by many different chemical modifications. It therefore seemed worthwhile to consider certain specific modifications of the functional group reactivity of feathers with reference to the effect of such reactivity on their filling power, ability to react with tanning agents, and their resistance to

microbiological deterioration. This latter property will be subordinated to the other two, and specifically investigated on those modifications which might offer promise by the first two methods of evaluation.

It has been noted previously that the amino acid composition of the feather keratin shows only one residue in five to contain acidic or basic residue, and further that some portion of the acidic residues is masked as the amide group. Hence, it seemed desirable to consider certain methods which might increase the carboxyl functionality of the protein. Lundgren (18) postulates that monothioglycol functions as a disulfide bridge rupturing agent which adds on to the protein an alcoholic residue. It was decided to try to combine the ability of acetic acid to swell proteins and the ability of thio compounds to break disulfide bridges by the use of thioacetic acid in the place of monothioglycol. The assumption was made that this agent would similarly add to the cystine disulfide bridge, resulting in a modified protein containing more carboxyl groups available for reaction with tanning salts such

TABLE III

INFLUENCE OF CATALYSIS CONDITIONS ON GLYOXAL MODIFICATION OF FEATHERS

Curl inducement	Glyoxal reaction catalysis	Filling power (cm.)
Tri-sodium phosphate—1%	Alum	4.6
Tri-sodium phosphate—1%	No alum—Phosphate in feathers	3.9
Acetic acid—0.1N	No alum—Feathers acid	4.2
Acetic acid—0.1N	No alum—Acid and neutral glyoxal	4.0
Acetic acid—0.1N	No alum—Acid and alkaline glyoxal	3.9
Tri-sodium phosphate—1%	Phosphate in glyoxal—pH 8	4.0

as the alum in the "Keracurl" process (6). Further, Olcott and Fraenkel-Conrat (21) have shown that phthalic anhydride reacts with egg white protein to give a significant increase in the number of carboxyl groups in the protein. Further, such reaction produced a significant decrease in the water absorbing ability of several proteins, although it did not do so on hog hair. Hence, data have been secured on the effect of two possible systems to increase the number of acidic groups in the protein.

Second, it was decided to consider reactions to remove the influence of the free amino groups of the feather. These are already small, and some additional information on a modified protein with even less amino reactivity might be informative with respect to the mechanism of the glyoxal reaction. The traditional method to decrease the amino functionality of a protein is through the use of nitrous acid. This reaction replaces primary amino groups with alcoholic hydroxy groups, and has some slight degrading effect on other basic amino acid residues. Hence, this reaction was applied to the feathers. Since it involves an acid reaction the treatment also provides a protein swelling reaction which might serve to distort the feather parts and give the necessary bulking characteristic. A second method of masking the free amino func-

tionality of proteins is by reaction with some acylating agent such as benzoyl chloride or phthalic anhydride. Therefore reactions with these two materials also could yield some information on the influence of amino group functionality in the establishment of the properties of the feathers.

Finally, it was decided to attempt to introduce a new functional group into the protein which might have more reactivity with tanning chemicals. The technique selected involves the coupling of the protein with a diazonium salt (4). The chemical selected for diazotization was sulfanilic acid, which would leave a free sulfonic group bound to the protein after coupling. This polar group should also be able to penetrate the coordination sphere of metallic tannages and provide an additional binding force for metallic tannages. Treatment with sulfanilic acid without coupling was also included to determine whether the mere introduction of bifunctional polar salt would significantly change the characteristics of the protein.

TABLE IV

INFLUENCE OF PROTEIN MODIFICATION ON THE CHARACTERISTICS OF CHICKEN FEATHERS

Protein modification	Tannage	Filling power (cm.)	Percent moisture	Percent nitrogen	Percent Al_2O_3 on N_2 basis
Chicken feathers—					
Control	None	3.0	9.6	15.0	—
Thioglycolic acid in EtOH	Aluminum acetate	4.0	—	—	—
Nitrous-chloroacetic acids	Aluminum acetate	4.1	9.2	14.4	2.5
Nitrous acid	Glyoxal ($ZnCl_2$ catalyst)	4.9	9.0	14.1	—
Phthalic anhydride	Aluminum sulfate	4.6	8.5	14.0	4.4
Benzoyl chloride	Aluminum acetate	4.0	9.1	14.6	2.8
Diazo coupled	Aluminum acetate	5.0	10.5	14.0	5.9
Duck feathers	None	5.0	—	—	—

Table IV presents results secured from functional group modification studies of feather keratins. These results are preliminary in nature; their significance will be indicated in the discussion portion of this paper.

The third portion of our laboratory studies involves investigations of the stability of the tannage given the feathers in the "Keracurl" process (6). This alum tannage is assumed to occur because of the penetration of carboxyl groups of the protein of the feathers into the coordination sphere of the aluminum salt. However, alum itself is not regarded by tannery chemists as a particularly stable tannage agent. Mineral tannages commonly take advantage of the ability of organic acids to enter the coordination sphere of the metallic tanning salt to produce a masked mineral tanning salt capable of giving a superior tannage. A commercially available aluminum actetate, stabilized with

boric acid, has been reported to give a superior retannage of vegetable tanned insole leather (11). It seemed logical therefore to compare the ability of this stabilized aluminum acetate to produce a modified chicken feather. Further, it was thought that this modified tannage should have superior resistance to the detannage during washing of the feathers, hence, the standard washing cycles to involve two repetitions of a one-half hour washing with one liter of a 0.25 percent solution of Igepal CO 630 per 25 grams of modified feathers. The filling power of the modified feathers, prepared both by the "Keracurl" process and the modified aluminum acetate process, was determined both before and after the detergent washings. Further, the aluminum oxide contents of the feathers on the nitrogen basis was determined on both types of feathers before and after the washing cycles. The aluminum oxide method involved the nitric acid destruction of the feather sample, followed by a colorimetric determination of the aluminum content of the feather digest, using aluminon (25). The traditional macro-Kjeldahl procedure employing copper catalyst was used to determine the content of nitrogen in the feathers.

Leather chemists customarily expect to secure a greater degree of tannage stability from a chromium tannage than from an aluminum tannage. There are two commercial systems of chrome tannage. The two bath process treats the skins first with hexavalent chromium in an acid solution, and reduces the chromium to the tanning trivalent salt within the protein by the use of sodium thiosulfate. This procedure is known to give a full plump leather, and is customarily used today on certain types of kid skin leathers. The one bath process reduced the chromium to the trivalent tanning complex outside of the skin, and then deposits this tanning salt within the skin by proper control of skin acidity. The mechanism of both tannages probably involves the penetration of acidic groups from the collagen into the coordination sphere of the trivalent chromium complex.

The work done by the Alexander Smith group in the development of the "Keracurl" process (6) had shown that chromic sulfate was able to give a modified feather equivalent at least to the alum process. However, the tannage conditions were not proper for best tannage stability, being too acid for proper chromium deposition onto the protein reactive surface. Therefore, an investigation of both one and two bath chrome tannage has been initiated, determining their influence on the filling power of the feathers, as well as upon the stability of the resultant tannages to laundering. A two bath chrome tannage applies the chromium to the protein in an acid dichromate solution, and hence it may also modify the feathers by conversion of the disulfide bridge of the keratin into an oxidized form. This additional reaction mechanism does not exist in collagen, where the two bath tannage is customarily employed, because the disulfide bridge is not present in collagen. Hence, it is possible that the comparative tannages of collagen and feathers by one and two bath chrome tannages may be dissimilar.

Tables V and VI present the data secured from the alum and chromium tannages. Table V considers the tannage stability and influence on filling power of certain differences in the aluminum tanning salts, while Table VI compares the filling power and fixation of either aluminum oxide or chromic oxide by the feathers when alum and chrome tannages are employed.

The work which has been carried out on feather modification has had one deficiency, in that the filling power test cannot reflect any of

TABLE V

STABILITY OF ALUM MODIFIED CHICKEN FEATHERS TO LAUNDERING WITH A NON-IONIC DETERGENT

Treatment		Filling power		Tannage level		
				Percent Al_2O_3 on N_2 basis		
Swelling agent	Aluminum salt	Before laundering (cm.)	After laundering (cm.)	Before laundering	After laundering	Percent detannage
Sulfuric acid	Aluminum sulfate	3.8[a]	3.8[a]	4.7	0.6	87
Sulfuric acid	Aluminum sulfate	4.1	4.3	5.6	1.3	76
Tri-sodium phosphate	Aluminum acetate	3.6[a]	3.8[a]	2.4	1.1	54
Two-stage phosphate	Aluminum acetate	3.7	4.3	3.3	2.4	28
Acetic acid	Aluminum acetate	3.9	4.1	1.4	0.9	39

[a] Aeration in filling power test may be inadequate.

TABLE VI

INFLUENCE OF TANNAGE CONDITIONS ON FILLING POWER OF CHICKEN FEATHERS

Tannage	Filling power (cm.)	Percent metallic oxide on nitrogen basis
Chicken feathers—Washed controls	2.9	—
Aluminum sulfate	4.1	5.6
Aluminum acetate	3.9	1.4
Two-bath chrome	4.3	9.2
One-bath chrome-acid swell	4.9	5.2
One-bath chrome-pickle swell	4.9	7.6

the possible deteriorative influences or different chemical treatments on feathers, unless these differences are very large. It is a static test, applying a very low load to the feathers; use of the feathers involves dynamic loading of the feathers, to much greater loads, and over many more cycles, so that the filling power test must lack sensitivity in the detection of mechanical deteriorative effects in the treatment of the feathers. It has been noted earlier that the barbs and the rachis originate independently of each other, and that the barb petioles and fibers thereof form the exterior layer of the rachis. Therefore it is logical to assume that the force required to tear the barbs from the rachis would be a sensitive indicator of any deteriorative changes. Further,

it is of course possible that the rachis itself may be deteriorated during treatment. Hence, it was decided to conduct a preliminary experiment to get some data on the error to be expected from such mechanical measurements of the feather properties. The availability of the Instron strain gauge tensile tester provided the necessary instrumental precision and accuracy for such measurements, so that the results obtained would enable us to evaluate the feather variability to be expected, and furnish the fundamental data necessary for the proper design of subsequent experiments. It was decided to compare the action of tannery unhairing agents on the feathers in this experiment, on the chance that these keratolytic agents might possibly modify the mechanical properties of the feathers. The data secured in this experiment comprise Table VII of this report.

Table III contains data on the filling power of lots of feathers treated with glyoxal under six different conditions of catalysis. The preferred reaction conditions in the original process reported by Frederick (8) involve the use of a tri-sodium phosphate curl inducement bath followed by the glyoxal fixation of the induced curl with an acid-alum glyoxal bath. These fixation conditions are the reverse of those normally considered proper for the fixation of aldehydes by fibrous proteins such as collagen. On the other hand, they are the proper catalysis conditions for fixation with acid amide groups (7) and for the fixation of glyoxal by cellulose (23). In view of the high level of hydroxy containing amino acids in chicken feathers, it is possible that this reactivity may be significant in the reaction between feathers and glyoxal. Hence, the experiments were designed to determine the influence of the catalysis conditions upon the ability of the feathers to yield a high filling power. It will be noted that the highest filling power in Table III is that given by the original process involving the acid-alum catalysis. Further, the high filling power secured in Table IV for the nitrous acid modified feather, fixed with acid glyoxal catalyzed with $ZnCl_2$, again confirms the conclusion that high filling power values result from the acid catalysis conditions, and particularly when metallic catalysts such as alum or zinc chloride are present. These then are the conditions known to favor reaction of glyoxal with hydroxyl groups rather than with free amino groups.

It is unfortunate that we have not been able to develop a method for the assay of the reacted feathers for bound aldehyde. This makes it impossible to assay the treated feathers to determine the extent of reaction which has occurred. Further, there is no simple test such as the shrinkage temperature test which is used in the evaluation of the aldehyde tannages of collagen to estimate the extent of reaction. Hence, it is impossible at present to make any attempt to quantitatively follow the extent of modification of the feathers which occurs in the glyoxal reaction. Hence, interpretation of the data must be limited; it seems that this topic justifies more extended consideration in future work.

Table IV presents data in which chemical modifications of the reactive nature of the feather substrate was attempted. The general philosophy of this approach has been discussed earlier. Briefly, it can be said that the amino acid analyses of feathers which are available suggest a rather low level of functional group reactivity, especially that of carboxy group reactivity which normally would be considered to be required for the fixation of metallic tannages such as alum by the feathers. The data in Table V will demonstrate that the stability of the deposited aluminum oxide in the aluminum sulfate treatment proposed by Florio (6) is rather low. It therefore was decided that modifications of the protein reactivity which would add an additional acidic group capable of coordinating to a metallic tanning salt would be reacted with the feather prior to tannage. It will be noted that in several cases the filling power secured was higher than we have been able to secure with our filling power apparatus from the aluminum sulfate modification of chicken feathers (Table V). Some of the reactions under consideration have received very little consideration, and the correct reaction conditions have not yet been obtained for maximum reactivity with the feather protein. The reaction which has received the most study has been that of diazo coupling of the feathers, in which diazotized sulfanilic acid was coupled with the feathers in the presence of 1 percent of tri-sodium phosphate (expressed on the hydrated salt weight basis). It is presumed that this reaction consists of direct coupling of the diazonium compound with the aromatic residues in the feathers; however, Eagle and Vickers (4) believe that free amino groups of many amino acids bind diazonium salts. Since this would result in the reacted feather carrying a sulfonic group which would be capable of penetrating the coordination sphere of a metallic tanning system, it would be expected that such coupling would increase the ability of the feathers to fix metallic tanning salts. It is noted that the level of aluminum oxide fixed with feathers modified by this reaction is greater than we have been able to secure with unmodified feathers, when both feather products are treated with the stabilized basic aluminum acetate. Further, these aluminum fixed, diazo-coupled feathers have a very bulky visual appearance, are brownish-red in color on White Rock feathers, and give a filling power under our test conditions equal to duck feathers. Further work is required upon the idea that reaction of the feather to increase the functional group reactivity of the feathers should increase the value of the feathers for use in sleeping bags, but these preliminary data are presented to show that the idea does seem to be feasible.

The conditions employed in the aluminum sulfate fixation of the feathers in the "Keracurl" process (6) are not optimum for the fixation of the deposited aluminum by the feather protein. It has been noted that greater tannage stability would be expected from the use of an aluminum salt of modified coordination ability. Table V compares the filling power and aluminum oxide fixation of feathers tanned with both aluminum sulfate and with aluminum acetate, both before

and after an arbitrary washing cycle. It is noted that the feathers tanned with the basic aluminum acetate retain a larger percent of their aluminum oxide after washing, and show a filling power measurement equivalent to that of the aluminum sulfate tanned, washed feathers. Since the ability of the feathers to withstand microbiological deterioration in service will be dependent on the stability of the tannage, these results are suggestive of the potential greater utility of aluminum acetate tannages. It is noted that the initial fixation of aluminum oxide is lower from the stabilized basic aluminum acetate than it is from aluminum sulfate. This is anticipated from the greater stability of the coordination complex of the tanning salt in solution, with a consequent slower penetration of the coordination sphere by the protein carboxy groups. Further, it is probable that a considerable portion of the aluminum oxide found in the aluminum sulfate modified feather has been physically deposited within the feather protein, rather than reacted with the protein. It must be recalled that the last step of the aluminum sulfate modification involves the neutralization of the aluminum sulfate tannage, with resultant precipitation of the hydrous oxide without reaction with the protein. Certainly the ready detannage of the modified feathers is suggestive of this assumption; it is very doubtful whether the hydrous aluminum oxide deposited on the feather protein during the neutralization adds materially to the stability of the aluminum sulfate modified feathers. These data are indicative of an approach to the control of the properties of the alum modified feathers which should receive further study.

It has already been observed that aluminum tannages on collagen are not as useful commercially as chrome tannages. Table VI presents data upon the comparative filling power resulting from the application of aluminum tannage and chromium tannage to feathers. It will be noted that the three chrome tannages give superior fixation of metallic oxide than has been secured from the use of aluminum tannages; this should give greater resistance to hydrolytic deterioration and microbiological attack of the feathers in service. Further, the initial filling power values secured are superior for the chrome tanned feathers than for the alum tanned feathers. Data are currently being secured on the tannage stabilities of these tannages.

Table VII presents the data secured on the influence of alkaline keratolytic agents upon the mechanical properties of chicken feathers. The weight increase, or swelling, data are consistent with the alkalinity of the solutions used and their chemical reactivity on keratins. The swelling levels with sodium sulfide solution (0.1N) and dimethylamine solution (1 percent) are noted to be particularly high. The greater alkalinity and keratolytic reactivity of these materials is recognized in tannery use as unhairing accelerators. The most striking feature noted in the mechanical property studies of the feathers is the rather large error or variability estimate given in the last line in the table. This error estimate was secured from the between feather variability

from feathers selected from the treated lot so that they were free of either the excessively large or excessively small feathers. However, the statistical coefficients of variability are still large. This is particularly true for the force to pull off the barbs and the breaking load necessary to rupture the rachis. As is customarily the case, the coefficient of variation is smaller for the two rachis extension characteristics, that is the force to extend 5 percent and the work recovered from relaxation of this five percent extension. These latter two factors are probably better measures of the rachis properties than the actual breaking strength.

It is possible that some of the variability in the rachis properties results from the fact that the same feathers used to measure the force required to tear off the barbs were also used to determine the

TABLE VII

INFLUENCE OF ALKALINE TREATMENTS ON THE FEATHER PHYSICAL PROPERTIES

Treatment	Percent weight increase (70 minutes)	Forces to pull off barbs (grams)	Rachis properties: Force to extend by 5% (grams)	Rachis properties: Recovered work from 5% extension	Rachis properties: Breaking load (grams)
Unwashed White Rock feathers.....	—	848	520	37	1030
Detergent-washed feathers	—	950	540	36	1080
Detergent-washed water-soaked feathers.	74	892	570	35	1745
Detergent-washed lime-swelled feathers..	99	918	550	36	2265
Detergent-washed sulfide-swelled feathers	133	798	820	36	1480
Detergent-washed sulfhydrate-swelled feathers	83	1017	580	38	1020
Detergent-washed dimethylamine-swelled feathers	127	778	540	33	815
Error as coefficient of variation—Percent	—	39	37	29	50

rachis properties. It is possible that the mechanical damage to the rachis from pulling off the barbs is greater than realized. Hence, in future work it seems advisable to accomplish a better fractionation of the feathers prior to testing, and to select separate feathers for each property to be determined.

In view of the rather large variability in these data, the statistical analysis of the data did not develop any strong correlations between property changes in the feather and the chemical treatment applied. It is noted, however, that the dimethylamine treated feathers have the lowest force to pull off the barbs, the lowest recovery of work of extension, and the lowest rachis breaking load. The sodium sulfide swelled feathers have a low force to pull off the barbs, but the rachis properties indicate a stiffened rather than a weakened rachis. It seemed from the fracture test that it rather than a tensile test might have demonstrated the effect of the sulfide treatment more sensitively.

This experiment is certainly not conclusive. It is presented here,

however, to record our belief that it is imperative to develop other test methods for the evaluation of the properties of the treated feathers to complement the filling power test. The inability of the filling power test to offer data relating to the fatigue characteristics of the modified feathers must be complemented with some form of mechanical stressing of the feathers. It is believed that continuation of work with the Instron tester will permit us to develop information of value on this question.

The work reported in this paper suggests that consideration should be given to the response of treated feathers to the exposure conditions encountered in the use of the feathers to complement the filling power test as a method of evaluation of the effect of a treatment procedure. It must be realized that the ability of the feathers to resist hydrolytic deterioration and microbiological deterioration during field use of the sleeping bags and their laundering will be concerned with the tannage stability, which the filling power test cannot reflect. Data have been presented which suggest that it is possible to modify the alum tannage by the use of a basic aluminum acetate to secure an alum tannage of increased tannage stability without sacrifice in the ability of the feathers to offer increased filling power. Further, chromium tannages seem to offer promise in this regard.

Further, it seems from the data presented in this paper that consideration of the particular amino acid composition of the feathers may make it possible to state the limiting conditions for the best modification of the feathers more carefully. It is suggested that the high content of hydroxy containing amino acid may influence the reactivity of feather with glyoxal. In any event acid and metallic salt catalytic conditions known to favor cellulose-glyoxal reaction seem to favor feather reactions, in counter-distinction to the normal reaction conditions used on other fibrous proteins such as collagen. Further, diazo coupling of sulfanilic acid and feathers has produced a feather which seems to have more reaction affinity for metallic tannages such as aluminum tannage. The resultant feather has very desirable feel and filling power properties, and it is suggested that further studies on the modification of the chemical functionality of the feather substrate would be productive.

Finally some preliminary data are presented on the action of keratolytic agents on the mechanical properties of the feathers. The heterogeneity of feather properties has prevented this experiment from being too conclusive. However, it is emphasized that the filling power test will not reflect the response of the feathers to the dynamic stressing they will receive in service, and it is felt that continued study of such tests can develop an additional method to be used in the evaluation of the modified feathers.

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Discussion

MR. LERMAN:

Did you run any filling power tests on these chemically treated aged feathers to compare them with the original in filling power you got from your chemical?

DR. LOLLAR:

We've been working on the project for five months. I also would say we've had considerable trouble getting a good filling power test; we could not get as large values as we should be getting. We have been continuously modifying our filling power test. However, I know of no evidence of a deterioration in filling power, but it might be there.

MR. LERMAN:

In one of the tests you had a high percentage of moisture when you had the chrome tannage test with five percent filling capacity. Isn't it possible to bring moisture content down to get greater filling capacity?

DR. LOLLAR:

You saw the curve presented in the paper just before mine; our measurements were made at 50% R.H. One thing I might say, however, with regard to this: the water holding power of the mineral tannages is a combination of holding power from unmasked groups of the protein, and the ability of the chrome to hold water. It would be possible to lower the water, but those results are always presented on a comparable relative humidity basis.

QUESTION:

We in the feather industry have had in the past quite a considerable time controlling odor and, under these conditions of tanning, the odor conditions have a great importance.

DR. LOLLAR:

In some ways, that's ahead of the place it ought to be. It concerns the papers Dr. Frederick and Dr. Florio are presenting tomorrow. The work we have done indicates the treated feathers are much less odorous, and they are free from unpleasant smell under humid storage

conditions for a long period of time—at least, for several days, the odor of the feathers is very good in comparison with the untreated feathers.

QUESTION:

Can you tell us the exact mechanics of your process?

DR. LOLLAR:

Well, as far as the alum tannage and the glyoxal work, I would rather let you wait until you've listened to the papers tomorrow which Dr. Florio and Dr. Frederick will present. I'll tell you a little about the chrome tannage.

The washed feathers in our case have been treated as the specification requires with detergents and the acid sour; they are dried down. Before processing, they are rewetted; then given a pickle for a half hour or so in pH 3 with 5% sodium chloride. Following that, a chrome tanning salt is added dependent upon the amount of uptake we wish to secure. It is added as a solution of a commercially available product approximately a thirty-to-one ratio of the water to the feathers. Allow that to drum for various periods of time. After that, the feathers are drawn off, tumble dried, then conditioned, stored, and tested. The reaction conditions are very nearly the same in chrome tannage as those Dr. Florio will be talking to you about tomorrow.

DR. KENNEDY:

I wonder if you'd elaborate further on the structure of this treatment as compared to others.

DR. LOLLAR:

Collagen should be contrasted to feathers. Consequently, the molecular structure, the stability of the feathers and collagen to swelling are quite dissimilar. Beyond the question of the disulfide bridging, the feathers are certainly not particularly over-blessed with functional groups which would promote typical aldehyde reactions conditions. It's our feeling that one of the things that would have to be done is increase the functionality of the protein. The reaction with the diazo compound, or treatment of the feathers with lime, decomposing the amido group—that type of reaction will increase the activity we believe. We believe the first increase in filling power comes from protein swelling.

DR. KENNEDY:

The principle changes that are taking place are in relation to the disulfide linkage?

DR. LOLLAR:

I haven't made up my mind whether we need to change the disulfide linkage or not. I am afraid if I change the linkage very much, I'm going to get a poor feather. To give an example, we had a two-bath tannage in which we gave too much chromic acid, which would oxidize the disulphide linkage. We certainly had a feather which looked nice and was very soft, but, even after tannage, did not have the filling power needed. I think there are two factors in this filling power.

Filling power is bulk; it is also resistant to compression. We have found it's impossible to increase the bulk without increasing the resistance to compression, just as though the feathers don't have enough guts to stand up under the load of the filling power. So, I'm inclined to think you want to maintain the disulfide linkage.

DR. KENNEDY:

Which amino acid are you going to attach it to?

DR. LOLLAR:

There are small quantities of basic amino and hydroxy-amino acids. I don't have reaction conditions for all that I'm satisfied with yet. Whether typical amino acid reactions have occurred, we don't know, but white feathers have turned to Rhode Island feathers in so far as color is concerned.

DR. KENNEDY:

Do you consider you are getting a lower extensibility?

DR. LOLLAR:

I notice first the dimensional form of the feather and then the resistance; I believe it has to do with the greater ability of each individual barb and barbule to resist deformation; I haven't done any barb extension testing along the idea used on wool. I haven't had the time.

DR. KENNEDY:

I want to find whether we have anything equivalent to cross-linkage.

DR. LOLLAR:

I have no reference for it in this case. I have some papers showing molecular weights decrease on aldehyde tannage of collagen. I would expect the same thing to be possible on these feathers. I believe your possibility is correct, but I don't have the evidence.

DR. KRIMM:

I really don't know what to say. It probably would be a little difficult to predict what the treatment might do. I don't know whether they'd expect it to remain intact or not.

QUESTION:

There are some papers show treated wool showed (INAUDIBLE).

DR. LOLLAR:

We have followed the papers very closely and some of the ideas and tannings we've used have come from those papers and I do feel that with increased cross-linking, stability of these feathers will be markedly greater when the feathers become dirty and soiled. I feel there is every reason to suspect this, because we've gone through this with leather, and I'm hopeful here we will find these feathers have increased resistance to microbiological deterioration.

QUESTION:

Since biological aspects have been brought up, most feathers are in some state of deterioration before they could possibly reach any processing plant. Is there any indication of the effect on the coefficient of the feathers? What effect would the condition of the feathers have on the results of your tests?

DR. LOLLAR:

We have no data on that. All of our work has been done on feathers secured at a poultry-killing plant, washed and dried the same day. I would say the more you let the feathers go to pot, the less chance you have to produce a good product.

MR. ARMSTRONG:

We have developed a treatment of sodium silico fluoride and we don't have any deterioration at all.

DR. LOLLAR:

That is essentially the situation we are using in our lab. Our lab is within a half mile of the poultry plant.

MR. KANE:

Mr. Weiner, you mentioned that in field use the underside of the sleeping bag is subjected to pressures up to three pounds per square inch. How does the filling power of the chicken feathers compare with down and goose feathers under such pressures?

MR. WEINER:

That's the unfortunate part of the behavior of these materials. Under low pressure, the difference between feathers and down and chicken feathers is quite great, but under three pounds per square inch, it's almost impossible to distinguish between them.

QUESTION:

Would that indicate for the underpart of the bag chicken feathers could be used now?

DR. KENNEDY:

That's a good question. I think it warrants a little more explanation than I tried to give this morning. I did not bring our inflatable mattress which will be used under extreme cold conditions. It's an air mattress used by the individual. We do anticipate that a man will improvise some kind of ground conditions under his bag—leaves or whatever he can get. The problem of the warmth in the bottom of the bag has always been one of our major problems. There is a real question—whether there's a bottom to the bag. During the war we had a group of explorers or mountaineers who had spent a great many nights in sleeping bags. It was their considered judgment that there is no bottom to the sleeping bag. We made the bags quite small on the theory the man would draw his knees up to a semi-fetal position and thereby assume a postion on his side and turn during the night as he felt cold. The difference between men of that sort and the average G.I. is probably considerable. As long as you are working with men who are used to sleeping bags, they learn to turn in the bag, and observations made of sleeping men using the bag show that they turn over when getting cold without awakening. Accordingly, the possibility of putting something in the bottom of the bag and saying we want something different there than in the rest of the bag presents a very considerable problem. We are studying the fundamentals of sleep at the present time, but have no definitive conclusions. There is a possi-

bility of constructing a bag with a bottom and not have it turn with the man. How to adapt a sleeping bag to a sleeping man is the problem. On that, we have no definite conclusions at this moment. If we were to come to the conclusion there is a bottom to the sleeping bag and we can control the men's habits to make sure they don't cool themselves off on one side to the point where they are no longer getting restful sleep, or they wake up, it would affect our whole approach to the problem.

In that case, we would probably go to a material with greater insulating value. The very use of the air mattress pre-supposes the ability of the man to turn over and stay on that air mattress.

Our basic objective, as I should have stated this morning, is to provide the third element in the man's protection—the third big element and the one on which far less work has been done than on the other two. On adequate nutrition, the first, we've done a great deal of work. The second is to provide protection while active, in the nature of clothing. The third, however, is to enable him to get sufficient rest so that he will be efficient over long periods—over months of exhaustive tension. To face an enemy with all the emotional and psychological problems attendant thereto, he needs the greatest amount of recuperation in sleep, the maximum number of hours, we can give him; particularly, to keep him from waking up. We try to give him rest, rather than just sleep.

QUESTION:

I have a question about processing materials chemically. As I understand it, you're trying to curl the feather. The rachis being the material of the largest diameter, probably your problem is one of attempting to direct reaction to one that's less reactive. Have you considered that problem?

DR. LOLLAR:

From my observation, I would say that great increase in filling power does not depend upon modification of the rachis, but upon the barbs. You will see that, after treatment, the barbs do not lay planar in configuration; nor do the barbules. It is true you will get a certain amount of conversion of vane barbs to look more like fluff barbs; it is true, under some conditions, you will get a curl or an actual spiral curl, in the rachis. It's been my observation, it's the barb increasing in volume that is important—as important, or maybe more important, than the curling of the rachis.

MR. CASSEL:

I was interested in the data that Dr. Lollar presented on the nitrous acid pre-treated, glyoxal tanned, chicken feathers. I'm wondering, since a lot of things can go on in this nitrous acid treatment, i.e., the hydroxyamino acid, tyrosine; the sulfur amino acid, cystine and the dibasic amino acid, arginine, are all affected to some extent as side reactions to the main diamination reaction; for this reason is it possible that it is the treatment with nitrous acid which increases the filling power?

DR. LOLLAR:

We have found that we do not get the marked increase in filling power at the end of the first bath. We have made it a practice to either dry the whole batch or a portion of the batch and measure filling power. The increase in bulk is often there at the end of the first treatment, but the increase in filling power is not there. I am inclined to agree with the solution Dr. Kennedy brought forth that it is a change in the mechanical quality which the change in the filling power requires. The treatment alone gives the bulk increase, but doesn't give the increase in filling power.

QUESTION:

What do you consider as the experimental error in your filling power?

DR. LOLLAR:

We know that, in the initial stages of the work, we don't get sufficient aeration. We had to put in gate valves and do a number of modifications. We are still a little bit low, I believe. We're going to check and see whether we or our treatments aren't doing as well.

QUESTION:

You had some showing filling powers of 3.9 and others better than 4.6.

DR. LOLLAR:

Perhaps I attached a little too much significance in the comparison. We have had pretty good reproducibility in most of our work. We've tended to run lower than we anticipated, but with better reproducibility. We have been using a "t" test type of analysis and I would be willing to say there was a difference of a half of a centimeter in filling power under identical test conditions.

DR. KENNEDY:

I'd like to make a statement or two somewhat in summary of what's been said today and keying it around the subject of Dr. Lollar's talk on the "Theoretical Considerations in the Chemical Modification of Chicken Feather Keratin." While we have present today the people who gave the very illuminating and stimulating papers this morning representing work at Cal. Tech and the University of Michigan and Dr. Low, I feel that we are going to have to find out what types of chemical modification in the protein structure can be achieved and what that will mean to our concepts of treatment. I am thinking particularly of the work of the Harris group on wool some years ago, and the work going on in the field of hair and wool today. I feel that to make real progress we will need to find out what kinds of modifications can be achieved.

QUESTION:

I would think that one of the things is the actual fibers; it seems rather surprising results in improvement are obtained after you've removed your amino.

DR. LOLLAR:

I have only two possible reaction mechanisms. One is that in which Dr. Lundgren's work suggested that the amido group of the protein reacted. Whether it was knocked off, I don't know. Second, the acid conditions involving the metallic acid catalysts, such as zinc chloride or alum, specifically, are found in the reaction with cellulose. These could be incidents proving nothing, but the fact still remains that the acid conditions do give the best filling power and I will look further into the action mechanisms.

QUESTION:

Have you tried other reagents, and have you any ideas how much ammonia was given off?

DR. LOLLAR:

We have not tried to study reaction mechanisms. When we get something more promising, we can study reaction conditions. We have worked with several other aldehydes and, of course, formaldehyde. I believe there was some work previously in Dr. Frederick's report with reference to the others. The work we have done on it is not far enough along to report at this time. I will say this; that as you consider the lengths of chain moving from formaldehyde to glyoxal to gluteraldehyde to different lengths of carbon groupings, you have an additional possibility of additional re-activities because of space-configuration; you have flexibility of properties that might result. You have also the cross-links from dialdehydes in comparison to formaldehyde. You have also the other aspect of the problem, as molecular size of the aldehyde increases the lack of the reaction in the close packed proteins coming into play. I certainly don't know that yet as far as feathers are concerned.

TECHNICAL SESSION NO. 3

DR. ADOLF SCHUBERT, *presiding*

CHAIRMAN DR. A. SCHUBERT:

The meeting will please come to order. The first paper this morning is by Dr. Patrick A. Florio on "Modification of Chicken Feathers Using the Acid-Alum Process." Dr. Florio is Assistant Manager of Chemical Processing at Alexander Smith Inc. He has been engaged on this problem for the past three years and his paper will present some of the very interesting results accumulated during this period. To Dr. Florio—as well as to Dr. Frederick—credit must be given for most of the work which shows possible practical value that has been done to date.

MODIFICATION OF CHICKEN FEATHERS USING THE ACID-ALUM PROCESS

PATRICK A. FLORIO

Alexander Smith, Inc.

I realize that I am faced this morning with two kinds of an audience . . . one technically skilled in the chemistry of protein structures and the other highly skilled in the art of handling and selling feathers. I'd like to point this paper towards the commercial people purposely excluding most of the measurements, treatments, etc., that have been worked on during the course of this contract and including only that data which supports the acid-alum process.

It is not until you have examined the physical properties inherent in feathers that you can begin to realize the reason for such a commonplace item assuming the proportions of a vital war material. Specific only to feathers, and more particularly those of waterfowl, they contain such useful qualities as high compressibility and resiliency, exceptionally poor heat transfer capacity, lightness in weight, high degree of bulking, and are naturally water repellent and fireproof. When put to use one derives a product that is warm, light, adaptable to weather changes, has great bulk and can still be compressed for easy carrying. It is no wonder then that this material finds its greatest potential in the wearing apparel of the more extreme climatic conditions, where man must be equipped with all these characteristics if he is to operate efficiently.

The availability of waterfowl feathers being what it is, the next product in line promising replacement is landfowl or, more accurately, chicken feathers. One of the reasons for this, of course, hinges on the supply and cost picture which, for this product, is ample and cheap. In comparing the two types, one finds that to a lesser degree landfowl

feathers likewise contain all the useful qualities heretofore mentioned. However, there are some morphological, structural and surface differences between them, which seem quite small but puts the two grades far apart in final performance. Perhaps the greatest of these, and the one we believe contributes the most to the beneficial effects of waterfowl, is that of feather shape. In appearance washed waterfowl feathers are invariably curled and fluffy with fibers extending in all directions around the center quill, thus occupying three-dimensional space and resulting in a large volume per unit weight, whereas chicken feathers are usually straight and flat and are easily susceptible to packing, resulting in a relatively small volume per unit weight. The shape is not only responsible for better bulking but also for other properties such as improved insulation due to the entrapment of larger amounts of stagnant air pockets in its non-oriented structure; improved resiliency and compressibility due to the ability of the feather structure to fold over on itself; and improved flow characteristics resulting from the ability of these bent structures to migrate within an enclosure, thus filling available spaces. With these thoughts in mind, the object of our work becomes clearly defined and that is to increase the bulking power of chicken feathers by the addition of a curl so that they could more nearly resemble their counterparts.

Fiber shape and yarn bulking are fields in which a carpet company maintains a perpetual interest, for these are characteristics basic to carpet construction. Our work on this problem, done under a Quartermaster Research and Development contract, was instituted to utilize our experience and to explore the possibilities of a Smith invention called the Textralizer. This machine, which consists of a stuffing box with a pair of feed rollers on one end and a weighted trap door arrangement at the other, is used to increase the yarn bulk by the addition of a series of "Z" crimps along the entire length of the fibers. It was thought that a modification could be made in this commercially successful apparatus in order for it to become applicable to feathers. Experiments were made using washed and unwashed, fractionated and unfractionated chicken feathers. The method of feeding the material into the crimping chamber was modified so that the feathers were wrapped in a pseudo sliver form in long, thin cheese cloth bags. In all cases the processed feathers contained sharp angular bends, and high percentages of broken quills. One of the problems encountered was that the action of the rollers caused irreparable damage to the rather soft pithy feather quills. To overcome this effect, the feathers were plasticized in dilute acidic and in basic solutions before crimping. The idea was abandoned when it became apparent that although feathers assumed a crimped position the filling power was not improved appreciably due to the high degree of breakage as well as matting that took place. Mechanical methods of feather bulking are doomed from the beginning because of the high incidence of breakage due to brittleness of the quills themselves.

Our next attack was the chemical approach. It was noted that when feathers are plasticized under an acidic condition and then neutralized a curl was imparted to the feathers on drying, which was not there originally and was not duplicated by a mere detergent wash. Attention was then directed to the possibility of causing this effect under controlled conditions. A series of acids, both organic and inorganic as well as acid salts and tanning agents, was investigated in an effort to obtain the optimum results from the standpoint of economy and ease of application in already-existing commercial plants. The outcome of this work was the process utilizing sulfuric acid and aluminum sulfate, trademarked the "Keracurl" ® process by Alexander Smith.

The treatment designed, as we said before, for commercial use consists of digesting the feathers for a period of one-half hour in a bath

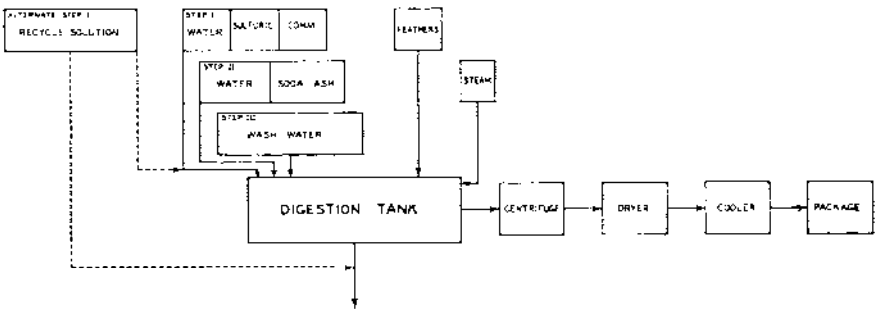

FIGURE 1

Flow diagram.

containing *2% by weight of total solution* of crystal grade sulfuric acid and 2% by weight of total solution of regular commercial grade aluminum sulfate or alum, at temperatures ranging from 140° F. to 150° F. This step is followed either by storing the solution for future use or by discharging it to the sewer. Warm water is then added to the digestion tank to replace the original volume and the temperature is again maintained at 140° F. to 150° F. A saturated solution of soda ash is then added slowly to the feather-water mixture until a milky color, due to the precipitation of aluminum hydroxide, is evident. The pH at this time is somewhere between 5 and 6 and the total mixture is agitated for another 20 minutes at these conditions. After this, the feathers are washed with cold water until the precipitate disappears, centrifuged by the regular methods and finally dried in a rotating type drier.

Figure 1 shows the flow diagram for the total process and the three steps involved in the treating cycle. The tank is first filled with water, then the acid added, then the alum, which may also be added in a solution form. The purity of these chemicals need not be critical. Feathers

are added last and the digestion started. At the end of this period the acid-alum solution can be reused if storage tanks and a recycling system are utilized. Our pilot plant work indicated that this solution can be reused up to 12 times without adversely affecting the filling power. Of course, slight additions of fresh acid-alum must be made each time to make up for the amount picked up by the feathers. Beyond 12 times it becomes impractical to use the solution due to the precipitation of dissolved protein and feather coloring matter. Without changing tanks warm water is added to make up the volume and soda ash to neutralize the excess acid and alum that may be absorbed onto the feather surfaces. The neutralization conditions are maintained for a period of time in order to make sure that this step is complete and that the final product is not acidic. The washing step is a typical industry procedure and may be aided with the use of a small amount of detergent. The centrifuge is likewise standard practice. The drying in this case must be performed without the use of constraining forces. We will speak of this in more detail a little later.

The process differs from the standard procedure only in the preliminary steps of digestion and neutralization. The heat involved in both steps is not in excess since feather washing in most commercial plants utilizes hot water. The biggest difference lies in the total time of treatment. The time elapsed here is about 1½ hours per batch up to the drier, as compared to about ½ hour in most plants. The product attained, however, can be directly compared to duck feathers both visually and bulk-wise. The "Keracurled" ® feathers are notably improved by virtue of increased fluffiness as well as the existence of a definite curl on the feather quill. In some cases the profiles have become almost circular in shape. This can be seen in Figure 2 which pictures the same weight of feathers before and after treatment. The filling density of untreated whole feathers (unfractionated) is increased from a figure of 1.8 to 6.0 cm. as measured on the Sinski apparatus. Figure 3 shows the typical improvements that can be attained from a variety of chicken feathers.

Although the highest filling power values are obtained from young, immature birds (18 weeks) the "Keracurl" ® treatment is not limited to these alone. Comparable improved filling powers are obtained from feathers previously washed in detergents or directly off the chicken's back. It has been possible to increase the filling power of feathers that were plucked three years previously as well as those directly from the chicken's body. While an attempt has been made to obtain comprehensive coverage, feathers from all of the chicken breeds which have been treated have responded to treatment.

Other beneficial effects of the treatment are the disappearance of odor, dirt and bits of skin adhering to the unwashed feathers. It has been found that feathers treated by this procedure exhibit a greater degree of water repellency over the untreated and over the washed duck feathers. "Keracurl" ® feathers kept at conditions of 70° F. and

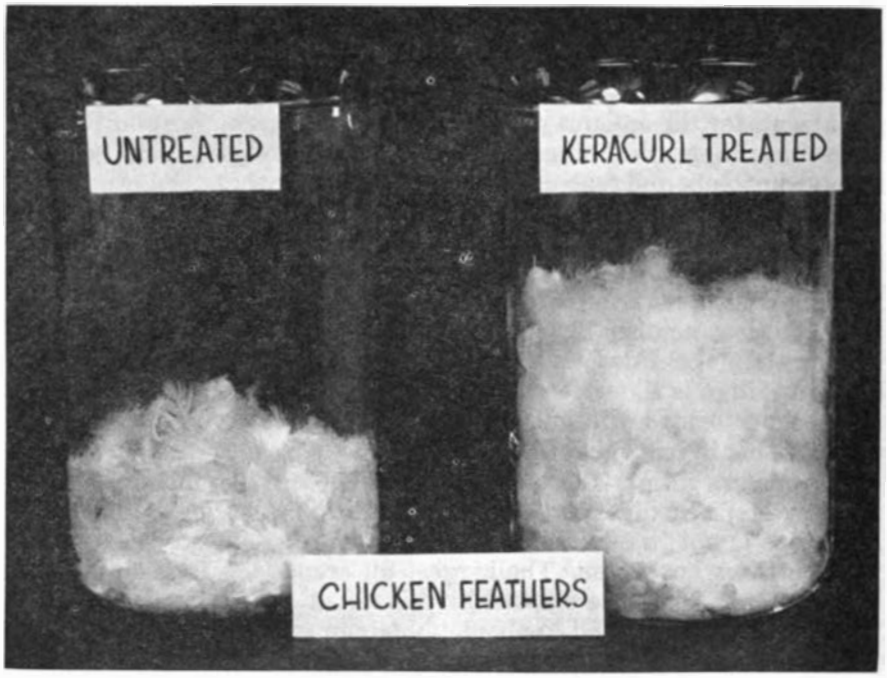

FIGURE 2

100% humidity for as long as two years have not become odoriferous nor have they shown any indication of putrefaction. This work has also indicated that this treatment can be used in place of the regular formaldehyde and detergent wash given feathers directly after plucking. And some work done at the Eisendrath Laboratories has shown that the rate of mold growth on acid-alum treated feathers is definitely reduced and in this respect they are better than the untreated duck feathers.

The "Keracurl" ® process will work satisfactorily on waterfowl

Description	Untreated filling power (cm.)	Treated filling power (cm.)
White leghorn	1.42	5.15
White Rock raw chicken—wet plucked	1.45	5.58
Grey barred Plymouth Rock raw chicken—wet plucked	1.40	4.97
Plymouth Rock	1.93	5.28
New Hampshire red	1.9	5.00
Delmar peninsula red	1.90	5.13
Red western	2.2	6.40

FIGURE 3

Filling powers of various chicken feathers

feathers as well as it does on chicken. Due to stock piling of such feathers over a period of time, it is often as long as five to ten years before a particular batch may find use in the finished product. During this time the bulking properties may be greatly reduced. The original bulking is not only restored by the use of this process but in most cases it is greatly improved. This can be seen in Figure 4 in which feathers stored for eight years were heated and the filling power was increased from 5.2 to 6.5 cm.

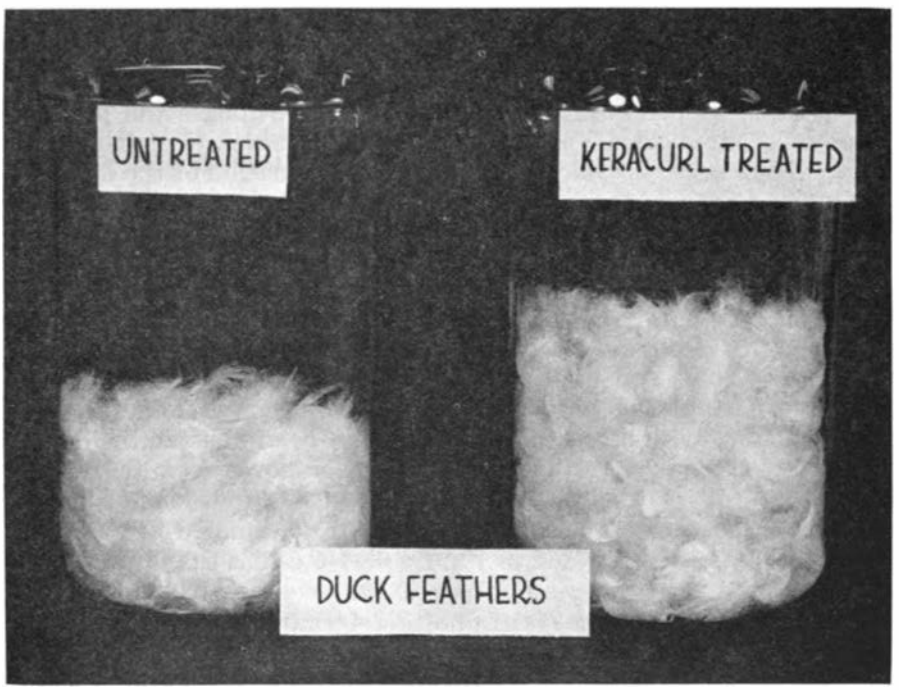

FIGURE 4

When calculating the cost per pound of feathers treated by this process there are a number of factors that are hard to resolve for us not in the industry. For instance, the price of raw materials will vary from place to place depending on the closeness to the feather source. Labor costs as well as maintenance costs will likewise vary depending on the location of the processing plant. Because of this, the only figures we can present with any degree of accuracy are those concerning the cost of chemicals and the heat input required to maintain the temperatures. Figure 5 indicates this, and presents the cost for chemicals per pound of feathers both for use of a one-pass method, using the acid-alum solution but once, and for the 12-pass system by recycling the solution. The figures appearing under the second column include the cost for the additional sulfuric acid and alum needed to replace the loss.

	One pass	Twelve passes
Alum	$4.92	$ .49
Acid	1.70	.20
Soda ash	.80	.06
Water	?	?
Total cost per pound of feathers	$ .0371	$ .0037

FIGURE 5

Chemical costs for the Keracurl Process based on the treatment of 200 lbs. of feathers in 400 gallons of solution.

After having obtained a visually successful product the next step in our research program was to compare and evaluate the product, using as a standard a known satisfactory material. Realizing that there existed no acceptable tests for the determination of the different properties to which these materials are subjected in actual use, our approach was to include the more empirical performance type tests as well as the more intense physical measurements.

The first of these was the laboratory washing tests performed on "Keracurl" ® feathers as compared to waterfowl feathers. This was done by first measuring the filling power of the feathers, then placing them into pillows and washing them, as is done in a home laundry, using Ivory soap. The pillows were then strung on a clothesline and allowed to dry, with occasional paddling in order to hasten the drying operation. After two days the feathers were removed from the pillows and relaxed for a period of 24 hours in standard conditions of humidity and temperature. The filling power was determined in each case and the results are indicated in Figure 6. Note that the filling power was decreased in both cases but only to the extent of 0.2 cm.

The next test performed was one to determine the permanence of the curl of individual feathers. A hundred treated feathers of various lengths ranging from two inches to four inches and containing a curl were placed between two wet towels and weighted down for a period of 24 hours. When the weights and towels were removed the feathers

	Filling power	
	Before wash	After wash
Keracurl feathers		
Pillow #1	5.2 cm	4.9 cm
Pillow #2	5.2 cm	5.1 cm
Pillow #3	5.2 cm	5.0 cm
Duck feathers		
Pillow #1	5.8 cm	5.6 cm
Pillow #2	5.9 cm	5.6 cm
Pillow #3	5.9 cm	5.6 cm

FIGURE 6

Keracurl feathers versus duck feathers

contained about a 45% wet pick-up and appeared flat and matted. Upon drying, however, they again became curled and fluffy to the same extent, it seemed, as the originals. In still another experiment for permanence the treated feathers, along with duck feathers, were placed dry in small cardboard boxes and compressed to a volume equal to 10% of the original. These boxes were then placed under different climatic conditions; one was placed in a home-type refrigerator, another was hung from the laboratory window and exposed to sun, rain and heat, and the third set was placed on the laboratory bench of an air conditioned room. After a period of one month the feathers were removed from these boxes, relaxed and the filling power measured. The analyses indicated no loss in the original bulking properties of either chicken or duck feathers.

Another practical test applied to "Keracurl" ® feathers is what we called a pillow test. An integral part of this experiment is a pillow the same size as the seat of an office chair. The shape of the pillow is square containing a partition diagonally across dividing it into two distinct sections. Twenty such pillows were made, ten pillows containing chicken feathers compared to duck feathers, five pillows comparing 40-60 duck down and duck feathers and 40-60 duck down and "Keracurl" ® feathers, and five pillows comparing "Keracurl" ® feathers and untreated chicken feathers. This test has been in operation for about eight months and we have failed to see any difference between the "Keracurl" ® feathers and the duck.

Another phase of the work done at the Smith Laboratories deals with physical measurements, with particular emphasis on establishing a correlation between filling power and specific physical properties. An attempt was made to compare duck feathers with acid-alum treated chicken feathers in order to establish whether the treatment increased the filling power by virtue of a stiffening action following the curl. In order to study this mechanism a bending modulus apparatus was constructed which consisted of a precision balance which was sufficiently sensitive to detect very small differences in the bending torque. In operation, this machine measured the force required to bend the quill to a given deflection. To establish the method a large number of measurements were made using random samples of a variety of feathers. The feathers dissected into their different components such as quill, barbule and fibril, were of different sizes and from different sections of the total structure. Reproducible results were possible only from the work on feather quills, other components being too soft and pliable. Final measurements were made on these, which constitute the major portion of the total feather weight. For the analysis, all fibers and side branches were stripped from the quill without damage to the main shaft, and then conditioned for three days at 70° F. and 65% humidity. The feathers used were of about the same overall length and the bending modulus was measured at the same distance from the base of the quill in all instances. Because of tremendous

variations that exist in the population of feathers, an analysis of this sort out of necessity becomes statistical in nature. To determine the trend it was necessary to analyze more than 100 feathers for a total of 600 readings.

The data obtained is merely an indication that the quills of duck feathers have a tendency to be two or three times stiffer than those of chicken feathers. It was not possible to distinguish between the treated and untreated chicken feathers.

Textile fibers have sufficient resiliency to return to their initial state after being stretched a certain percentage of their length. A measure of this stress-strain property often reveals differences and information valuable in the classification of fibers such as wool. Because of the likeness of wool to feathers, a similar study was undertaken. It was experimentally established that chicken feathers could be stretched to over 3% of their original length several times without any mechanical conditioning if allowed to relax between elongations. The force necessary for 3% elongation was arbitrarily selected to determine the effect of "Keracurl" ® treatment of chicken feathers. Selection and testing of the feathers was carried out in the following manner: Feathers of approximately the same size (3″) and shape were selected, and from these were culled all members which did not have a specific quill diameter at a distance one inch from the quill base. After suitable relaxation at standard conditions of temperature and humidity the individual feathers were extended on the tensile tester to 3% elongation. The corresponding 0.02″ length of quill was stretched in each of 20 specimens. The force required was determined for each feather and the average value calculated for the set. The feathers were conditioned and then stretched over the identical lengths again until statistically correlative results were obtained.

Four sets of 20 feathers each were examined in this manner. Each group was elongated until two average force values correlated; then the sets were subjected to some degree of acid-alum treatment. The resulting feathers were conditioned in the usual way, then elongated as before until two average force values agreed. The four sets were classed as no treatment, under-treatment, over-treatment, and standard treatment. On the basis of careful selection of individual feathers, careful control of elongation, testing and statistically sound analysis of the numerical data, all the groups remained unchanged within the limits of the test method, indicating that the treatment does not adversely affect any elastic properties the feathers may have had originally.

A study was made to determine whether the strength of the bond existing between the barb and the quill was weakened by the "Keracurl" ® process. Weakening of this bond would cause the barbs to separate from the main structure resulting in greater quantities of so-called "fly" and thus detracting from the bulking power of the material. Reduced to physical terms this property could be measured as the force necessary to pull the individual barbs free of the quill.

Feathers of approximately the same overall size and shape were selected and mounted in a special jig constructed for use on the tensile tester. With the quill clamped in a horizontal position the barb, held in a vertical chuck, was then pulled free of the quill. Five to ten barbs were extracted in this manner from one side of each feather, while the force to do this was measured on the Brown Recorder. These same feathers were then subjected to the regular "Keracurl" ® process. After treatment the extraction procedure was again repeated, using the barbs opposite those already pulled and clamping the quill as before.

The average values for the force required in each case were determined for a set of two feathers. Statistical treatment of the data indicated no change had occurred in the breaking strength of the barbs.

Despite the optimistic results obtained from all these tests we were still faced with the problem of the evaluation of this product in terms of true filling power. We reasoned that since these materials are used for long periods of time under repetitive conditions, that a proper test should include the properties of compression, resilience and time. Of necessity then, the term filling power, if it is to be used for determining performance characteristics, should represent the average of many cycles of compression and release and not just the initial bulk. To do this we have designed and built a machine called the compressometer, a diagram of which appears in Figure 7. This apparatus works automatically, and is composed of a plexiglass cylinder which is secured to the base, a calculated weight which exerts a pressure of 0.5 lb. per square inch, a mechanism for the gradual compression and release of the weight in relation to the charge, a timing device and counter, a calibrated scale for the determination of bulk, and an air nozzle adjusted to work intermittently and used for stirring feathers.

In operation 25 grams of feathers are placed into the plexiglass cylinder and the operation started. By virtue of a cam arrangement, and the loosening of the tapered screw, the weight is progressively applied until the feathers can support the total weight. At this time the tapered screw becomes engaged directly with the cam arm, preventing the further downward weight motion. By this system the feathers are compressed with the same weight each time and should the bulking level decrease, the weight will adjust to the new height. The cycle can be made variable but consists of compression for three seconds, and release for 15 seconds. The air nozzle located at the base of the cylinder stirs the feather charge every five cycles to prevent any packing or matting on the part of the sample and also to accelerate the test. Without this latter feature the test would go indefinitely. The bulk which is measured on the cylinder when the load is applied is correlated to the Sinski apparatus and is measured every 500 cycles and plotted as the minimum thickness versus the number of compressions. Since starting these tests we have had examples of materials

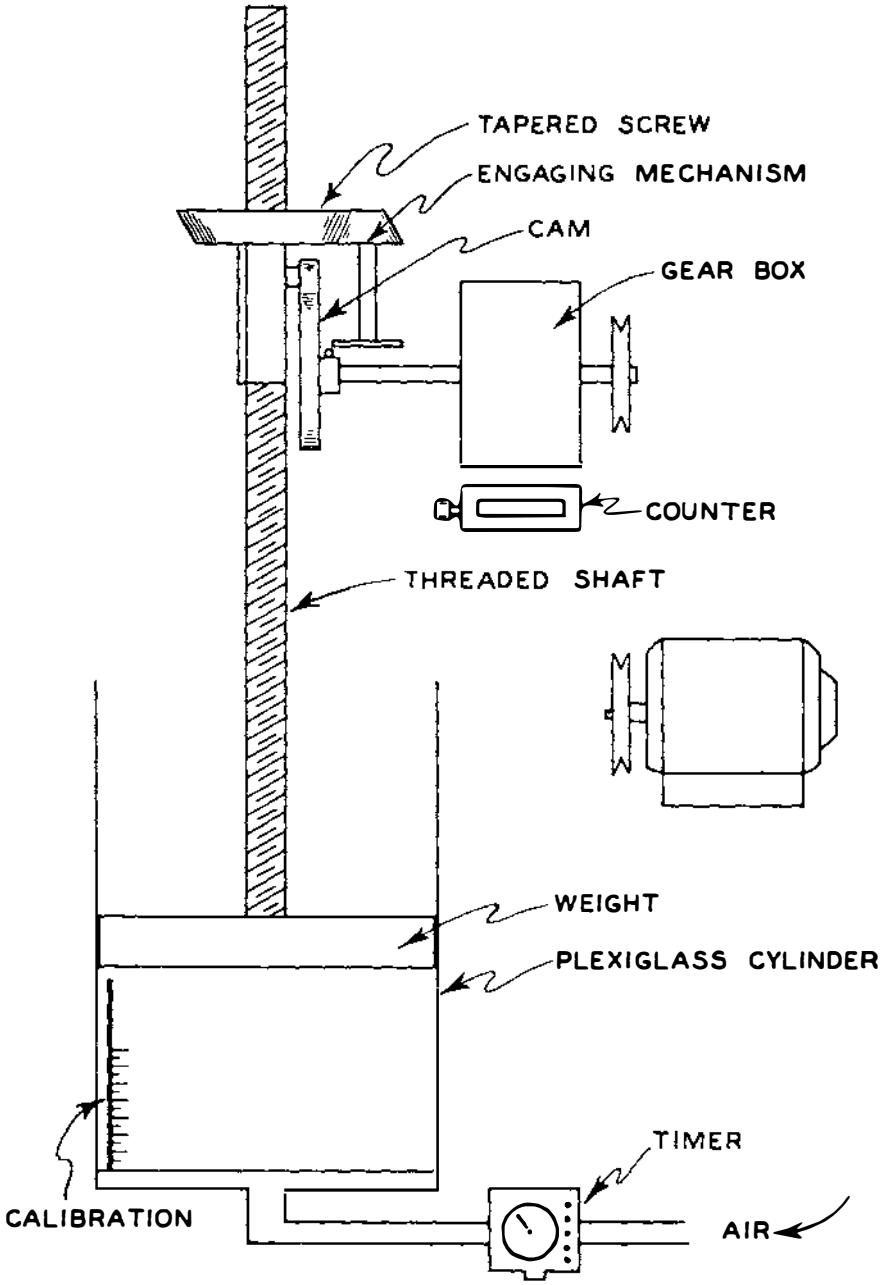

FIGURE 7

Compressometer

that show good initial Sinski filling powers but have subsequently shown poor compression due to matting and breakage; on the other hand, we have had samples showing only fair filling powers that have retained this ability to bulk even under extended compressions. In all cases, however, the true filling power seems to be somewhat lower than suspected. Figure 8 indicates average curves obtained for four different levels of filling power. Notice how the curve for untreated chicken feathers drops soon after 500 compressions have been applied. The others maintain a rather steady level. Figure 9 likewise shows a comparison between treated chicken feathers and untreated after 10,000 cycles. Again you see the sharp drop in the bulking of the untreated whereas the "Keracurl" ® feathers maintain a more or less steady line. Figure 10 shows the point already mentioned as to the apparent ability of some materials to show good filling power on the Sinski and then lose the ability on successive compressions. Note the sharp drop-off of second-hand duck feathers, which indicated a good filling power at the beginning. This effect could not be picked up on the Sinski.

Although this work is only preliminary, it is our intent to continue this kind of analysis since we believe it could make a real contribution to the art of measuring the bulking ability of not only feathers but of other filler materials.

The possible acceptance of the "Keracurl" ® process by the feather industry with a minimum of equipment changes or additions was one of the objectives considered in planning the commercial procedure. In line with this thought we would like to answer the question of just what is involved in adapting the "Keracurl" ® process to already-existing plants, by presenting a brief and simplified picture of the changes.

The existing method of washing as done in most plants is in a horizontal positioned tank, 500 gallon capacity, having a screened bottom which immobilizes approximately one-fourth of the total liquid capacity. Agitation is furnished by a rotating shaft which extends the length of the tank and contains paddles at staggered intervals placed radially along the length. The finished product is removed through a hatch on one side of the tank. Figure 11 shows this tank with the modifications that are needed to make it operable. Since we are converting to a system that is slightly acidic and at moderate temperature, the tank, as well as the stirrer, will need to be coated with an acid-proof paint or resin. A steam jacket will have to be welded to the tank in order to supply the heat needed to maintain the temperatures during the digestion and neutralization steps. This job can also be done by the addition of a lead coil carrying steam, if it can be worked so as to avoid the impingement of feathers during stirring. The heat requirement is an important function in the correct method of performing this process; it need not be an expensive item, however, since most plants already use hot water in the washing procedure and the heat supplied here is merely equal to the heat loss during the

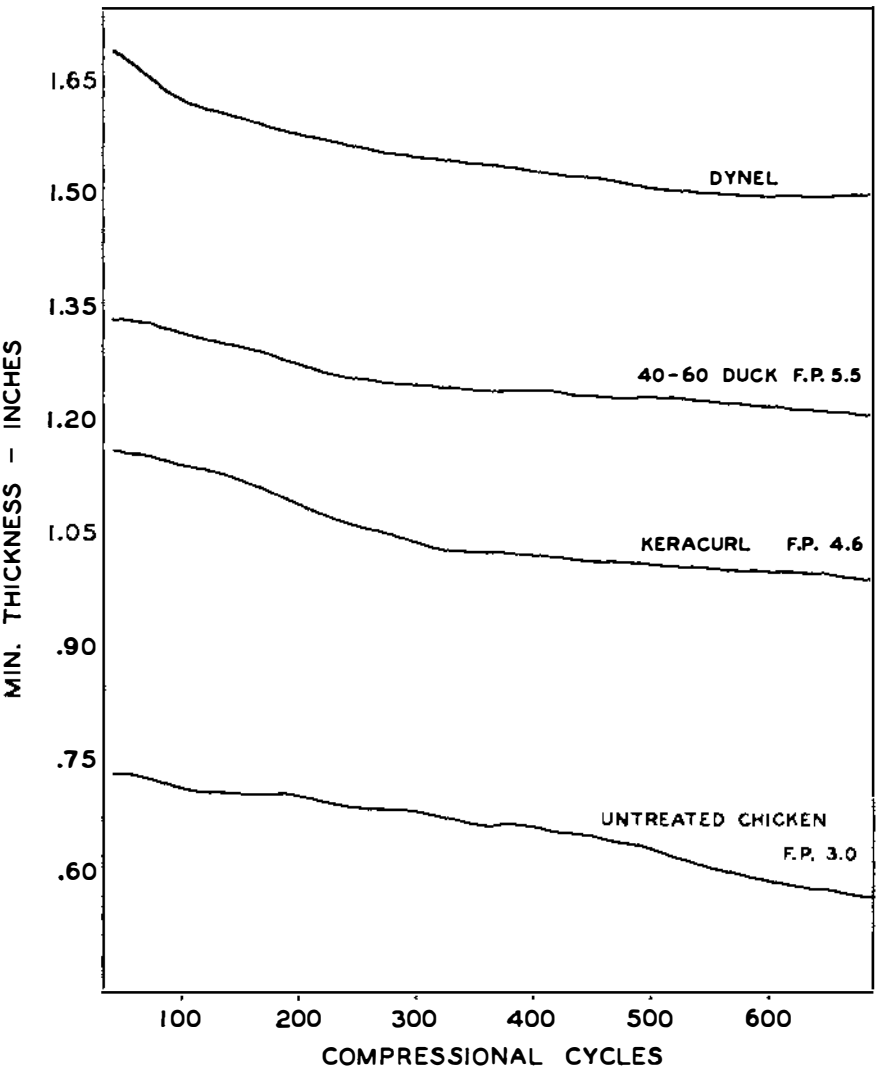

FIGURE 8

Compression Test

½ hour agitation. Figure 12 gives two cross-sectional views of the tank showing the two welded steam jackets, connecting lines and drain-off stopcocks.

An extraction step follows the washing in present operation and the same methods of handling apply to the "Keracurl" ® process. The usual method of drying by present procedures utilizes a horizontal tank, steam jacketed, containing a port hole on one side for batch feeding and a vacuum line on top to remove the feathers as they

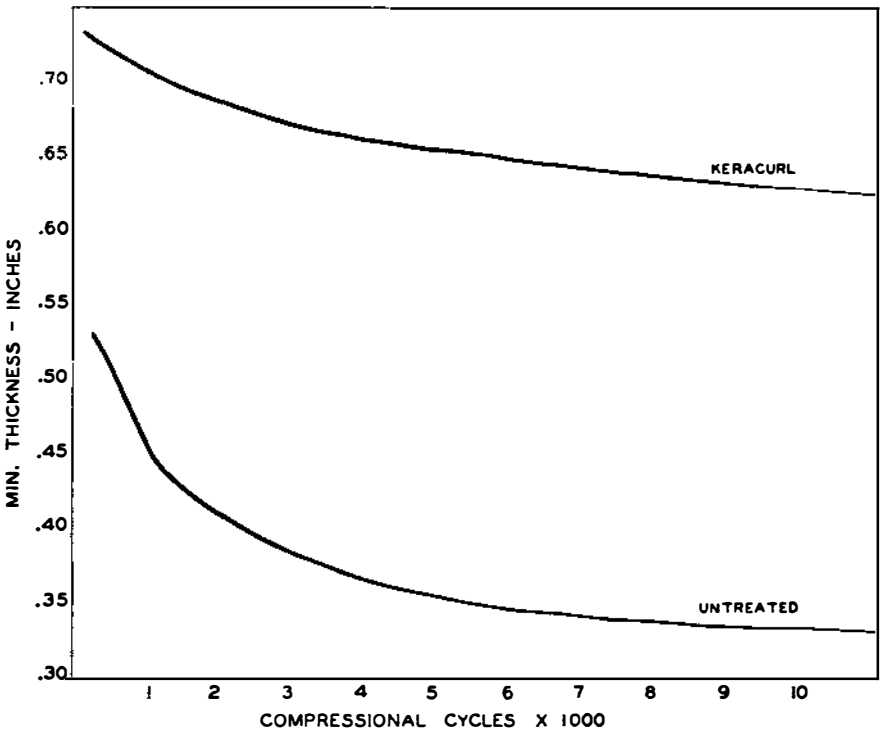

FIGURE 9

Compression Test

become dried. The wet feathers are stirred in this tank by means of a rotating paddle which churns them around until they become air-borne.

We have found that one of the most critical steps in the proper treatment of these feathers is that of drying. It has been postulated that the mechanism by which curling and fluffing occurs in the treated feathers is by the alternate swelling and deswelling of the feathers and quills as the pH changes from acidic to neutral, or that the treatment acts to open some of the salt linkages, allowing aluminum to react with the carboxyl groups, forming an insoluble soap and at the

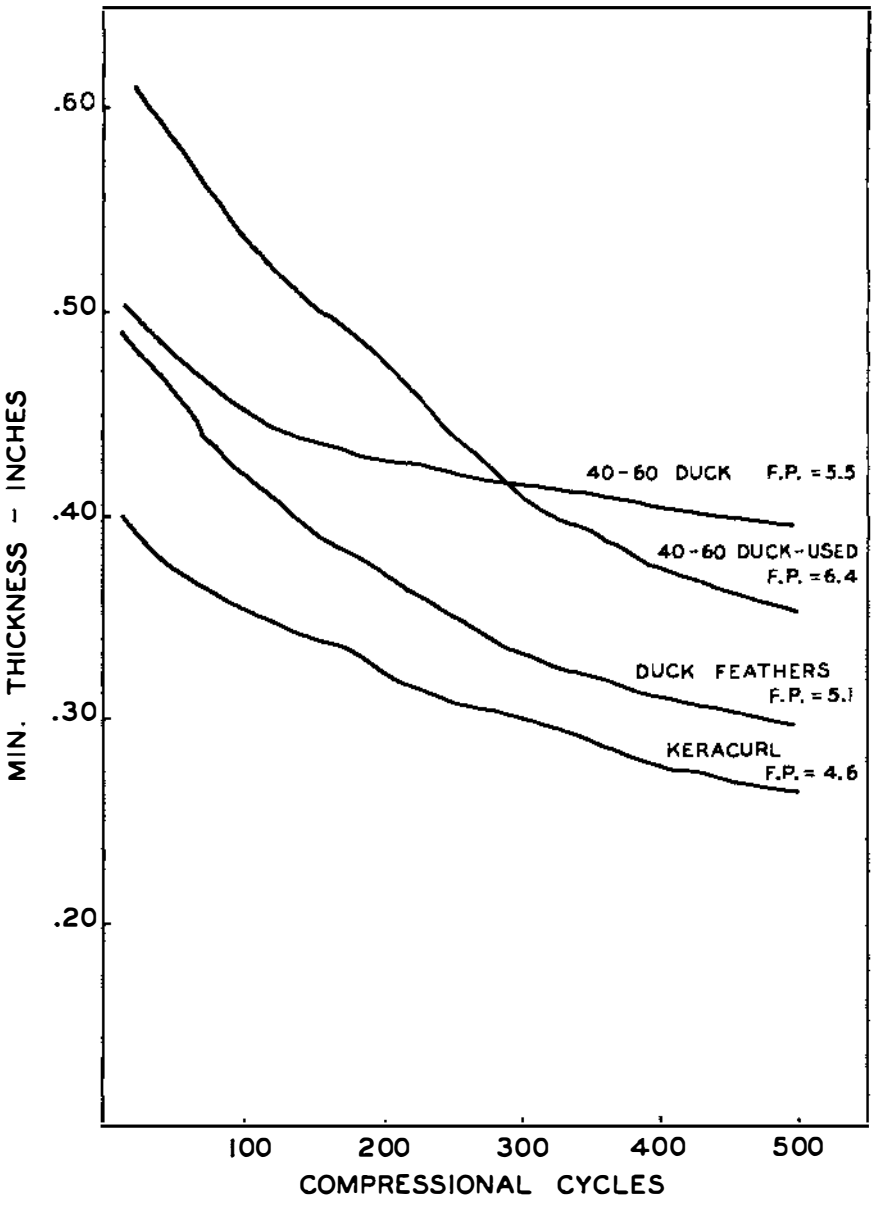

FIGURE 10

Compression Test

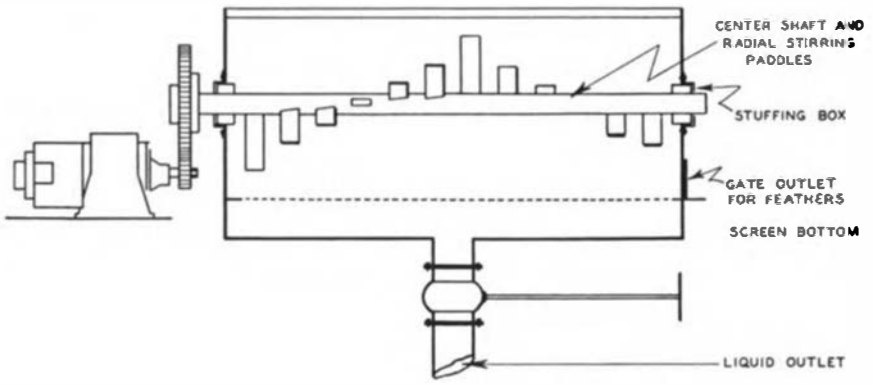

FIGURE 11

Digestion Tank

same time reducing the space between the side chains. In any case, the acid-alum either causes strains to appear in the structure or relaxes the strains which were there originally, resulting in deformation or curling. Since the feathers are in their most plastic condition just before drying, there is need then to perform this step without any constrainments. The product should be allowed to tumble in sufficient space in order to assume any position its internal stresses allow. To do this we recommend a tumble-type device of the variety used by feather processors in drying offal. Figure 13 shows a schematic drawing of a drier designed especially for this process. Note that this is a continuous operation where the feathers are placed in one end and continuously removed. The heat is supplied by an aerofin heater and the hot air moves across the chamber to the vapor exhaust. There is an added chamber at the end which cools the feathers by sucking in

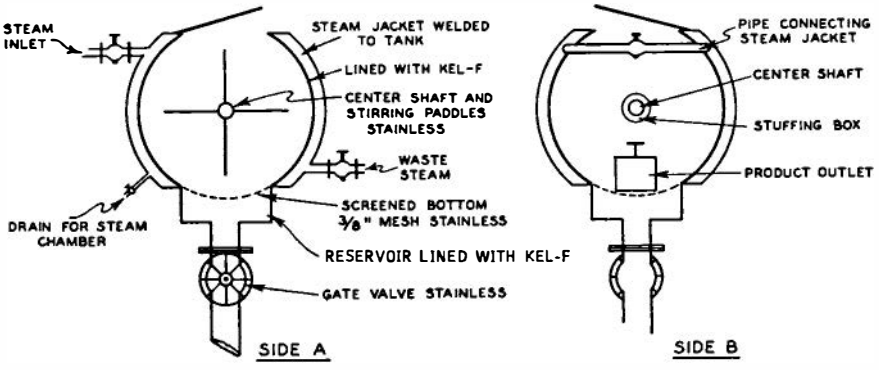

FIGURE 12

Cross Section of Digestion Tank

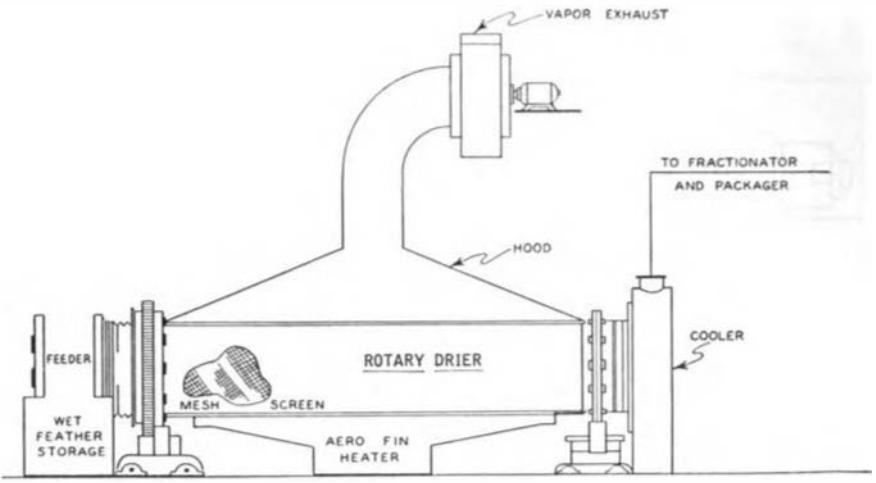

FIGURE 13

Schematic Drawing of Drier

cooled air and transfers them to the fractionators and subsequent packaging.

Figure 14 shows a drawing of the proposed layout. For purposes of efficiency, a number of storage tanks have been added to handle the sulfuric acid, saturated alum, and the saturated soda ash solutions. There are a number of variations that can be made here. The acid and alum can be concentrated into one tank, or they may be added separately, the alum may be handled in solid form, etc. If a recycle system is used, then a line is needed from the outlet of the digestion tank to a storage tank, which is either made of steel and resin coated or out of stainless. The rest of the layout is familiar, with a centrifuge, drier, cooler, fractionator and finally packager. We have had practical experience using this process in a number of commercial plants and have found that it lends itself easily to application. We have not had the experience to operate a drier such as we suggest on

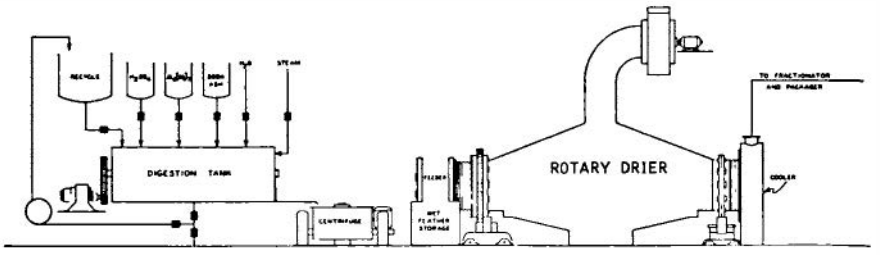

FIGURE 14

Schematic Drawing of Plant Layout

large scale, however, a scaled-down model used for laboratory runs indicates commercial feasibility.

It is wrong perhaps to assume at this time that "Keracurl" ® treated chicken feathers can immediately replace or substitute for duck feathers in all instances. It is possible, however, to use these feathers as diluents for the more expensive materials and still not decrease the resiliency or buoyancy of the article and without the necessity of using a greater quantity by weight than is required when all waterfowl

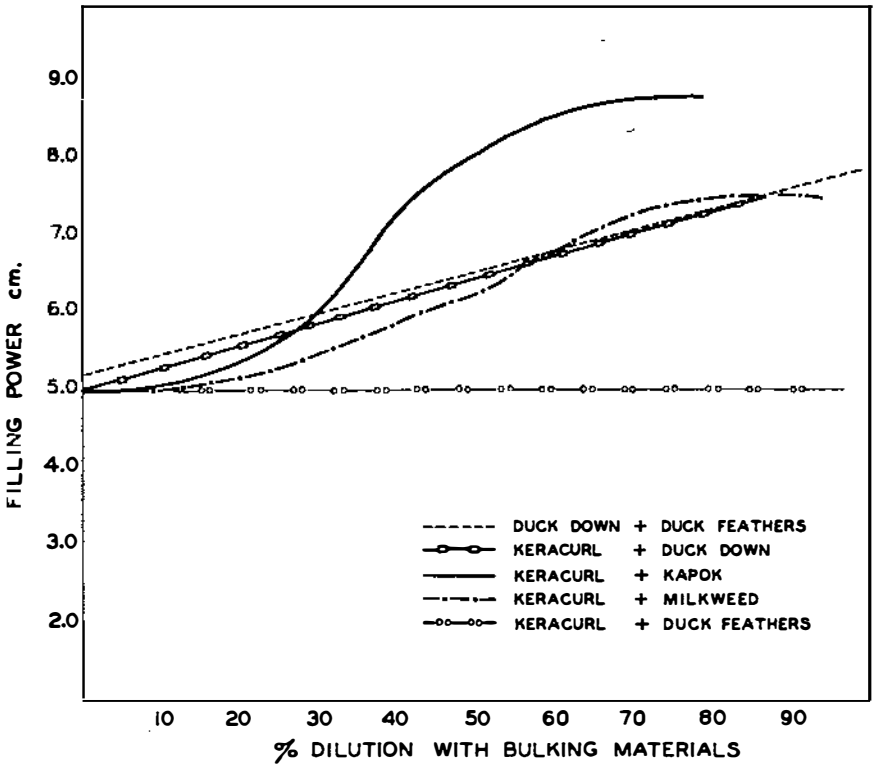

FIGURE 15

Dilution Studies with Keracurl Chicken Feathers

feathers are used. Dilution studies at our laboratory, as shown in Figure 15, indicate that duck feathers may be diluted up to 90% with "Keracurl" ® feathers with no loss in filling power. As a matter of fact, it is hard to find the "hand" differences between a blend of 60-40 waterfowl and down and one containing 40 "Keracurl" ®, 20 duck, and 40 duck down.

In our dilution studies we have also included other materials in an effort to replace down. These included milkweed, kapok and dynel. It is interesting to note that mixtures of 60% "Keracurl" ® feathers

and 40% milkweed gave a filling power of 5.7 cm.; that 60% "Keracurl" ® feathers and 40% Kapok gave a filling power of 6.3 cm. and the same ratio using 40% duck down gave 5.9 cm., as compared to 5.9 cm. for the 60-40 duck feather and down.

It becomes obvious by the data presented that the use of these feathers offers three distinct commercial advantages:

1. The use of a substitute material in place of the more expensive and critical ones such as waterfowl.
2. Reduction of stock piling due to the increased volume of available materials.
3. Improvement of stored materials, making it possible to effect a saving by the use of less material per unit volume.

During the course of this talk a new treatment for chicken feathers, trademarked The "Keracurl" ® Process, has been disclosed. It is possible by the use of this method, which utilizes a dilute solution of sulfuric acid and alum, to increase the filling power of chicken feathers to the level of duck feathers.

Physical measurements, which include bending modulus, stress-strain and barb pulling have not disclosed any deleterious effects due to the treatment. Compression tests have shown an improvement in the resiliency properties of the treated feathers over the untreated. Even more practical tests such as laundry washing, permanence and pillow tests have shown that the treatment is permanent under ordinary conditions. Besides imparting a curl and fluffiness to the feathers, the treatment also improves the water repellency, removes bits of skin and dust, and increases the resistance to mold growth.

The commercial application in the form of the possible conversion of existing equipment to the use of the "Keracurl" ® process has been discussed as has the immediate commercial uses for the product.

CHAIRMAN SCHUBERT:

Dr. E. R. Frederick will present the next paper. It will be on the "Modification of Chicken Feathers by the Glyoxal Method." Dr. Frederick is with the Mellon Institute of Pittsburgh. He has been engaged in research work on fibers for the past eleven years; at present on a fellowship of the Albany Felt Co.

MODIFICATION OF CHICKEN FEATHERS BY THE GLYOXAL METHOD

E. R. FREDERICK

Mellon Institute of Industrial Research

Although the title of this paper is rather specific as indicated, I should like to include a brief résumé of some of the other activities in the studies of chicken feathers, primarily to illustrate the background for the chemical altering process and perhaps also to stimulate interest in other developments of potential significance.

Naturally our objectives in studying filling materials for sleeping bags, like those of other investigators, were to devise a high bulk insulation medium of domestic origin that would be applicable as a replacement for waterfowl feathers. Of course this implied the need for a study of corrective modification processes for chicken feathers, but did not exclude the examination of fibrous materials. Chicken feathers, therefore, were given first and foremost attention and any other high-bulk media was to be considered of secondary importance.

At the beginning of the program considerable emphasis was placed upon the natural surface finish of waterfowl feathers and down and this led to an extensive survey of additives, cleansing methods, and treating processes as applied to chicken feathers. While these investigations confirmed some hypotheses and served to indicate differences among waterfowl and chicken feathers, the means for achieving significant bulk improvement by surface add-on alone were found to be rather unsatisfactory from the standpoint of durability. Consequently, later studies were devoted to physical and chemical form modifying operations in order to obtain the high bulk improvement necessary in upgrading chicken feathers.

The overall needs of a filler for use in sleeping bags have been indicated previously by other speakers. Perhaps at the risk of excessive repetition, I would like to review the requirements briefly noting the important differences between waterfowl and chicken feathers and then finally comparing the end product of our work with those requirements which we deem necessary in a filler for sleeping bags.

If we assume, and we can do so with a rather safe degree of accuracy, that bulk and insulation value are proportional, we will note that high bulk is an outstanding requirement of a filler for sleeping bags. We can also observe that this feature is lacking in chicken feathers. Now, if we overlook the down which probably owes its bulkiness to several factors including stiffness and the unique physical construction, we will observe that in feathers the primary visual difference between the two classes of feathers is the shape of the particles. Waterfowl feathers are more or less curved, that is the quill is curved, and these curled particles will return to this three-dimensional form even after distortion. Chicken feathers, however, are rarely curled and if they become curved in some course of the operation of processing, they will only retain the curl if no disturbing force is applied. This three-dimensional shape, then, of the waterfowl feathers accounts for their outstanding bulkiness and insulation value.

The next property of rather interesting importance and significance is that of drape in sleeping bags. The exceptional drape properties required in sleeping bags apparently can best be achieved through the use of relatively small, soft and discrete particles. Feathers and down fulfill this requirement rather effectively, while most fibrous, batt-type fillers ordinarily tend to influence drape adversely and unfortunately loose fibrous materials tend to result in a non-uniform distribution fill condition.

While waterfowl feathers and down do not resist compression to an outstanding degree, and this is one of the principal limitations of the filler, they do possess outstanding resiliency which accounts for essentially complete bulk recovery after they have been packaged or subjected to constant application of loads such as would be the case in use or during the rolling of sleeping bags for transportation.

Quite obviously if a filler were to be so sensitive to moisture as to become less bulky, less resilient, or in any other way less efficient insulation-wise, it would not prove satisfactory for use in sleeping bags. Although waterfowl feathers are not in themselves entirely water insensitive in that some water is absorbed, the changes occurring during reasonable periods of use are not so significant as those noted ordinarily for chicken feathers. Chicken feathers or any other potential substitute for waterfowl possessing other desirable characteristics must also resist physical and chemical degradation in the presence of moisture.

Any item of cold weather clothing may be exposed to open flames needed in the Arctic for warmth and cooking. Very flammable fillers, naturally then, must be avoided. The substitution of chicken feathers for waterfowl feathers would not be considered ordinarily to introduce a flammability hazard unless the altering technique or some special finish changes the burning characteristics of feathers.

Any item of military equipment must be considered eventually to be exposed to rather severe conditions of wear and require a laundering or some other cleansing operation. Laundering, of course, is much more practical in field operations and we must consider that a water-type cleansing operation will be applied to the military gear as a method for cleansing the garment. Whether in use or in storage the filler will frequently be exposed to humid atmospheres and for this reason the filler must resist degradation which could normally occur in the presence of moisture. It must retain its high bulk properties after repeatedly being exposed to compression that occurs in use or as a result of packing for shipment. Waterfowl feathers are more sensitive to degradation by microorganisms than actually desired, but ordinary chicken feathers are even more easily degraded and it is urgently recommended that an improvement in bacterial resistance be achieved in either waterfowl feathers or a modified chicken feather sleeping bag filler.

Naturally, one reason for considering chicken feathers at all is that these products are available from the American poultry industry and therefore can be provided in considerable quantity. The demand for waterfowl feathers in an emergency requires importation of the raw material and therefore we depend on a rather unpredictable source of supply. We do have plenty of chicken feathers, probably at least 200 million pounds annually, and they are now priced right to offer an interesting material as a waterfowl feather replacement.

There are indications that outstanding electrostatic properties are

exhibited in waterfowl feathers as used in a bag to serve during fluffing to increase bulk properties.

Edelman had curled feathers some time ago by forming the particles over a mandrel using steam to effect the necessary plasticization. The resulting end product had a distinct curl that was effective in increasing bulk properties. Although improvement in bulk power was realized, the product did not retain the curled form unless steam was applied and under these conditions considerable embrittlement was noted. For this reason the entire process was considered impractical.

Ordinary chicken feather processing operations, as carried out in the feather plants, do not yield curled feathers, or if curling does occur in the course of the operation, the form is not permanent. The fact that chicken feathers would curl by normal processing was not ordinarily recognized until some form stabilizing process was developed. This is quite natural because as any curled, unstabilized product is exposed to moisture and compression stresses, it takes on the new form and loses its high bulking characteristics. Perhaps another reason for failing to observe the natural curling tendencies of chicken feathers is the fact that mostly mature feathers have been processed in the plants. Actually, military specifications call for mature feathers and now we know that these types of chicken feathers are more difficult to curl than the immature variety. Accordingly, it was not until we confined our investigations to immature chicken feathers and in addition were able to achieve some permanence in the curled form, that we found these inherent curling tendencies to exist. The explanation for curl development was considered to involve swelling and possible elongation with subsequent shrinkage occurring during relaxation drying. This hypothesis for feather curling appears to explain the operation taking place in chicken feather form modification and has results in methods for curling mature as well as immature feathers. Although the swelling-contraction mechanism seems to explain curl development in chicken feathers, other factors may influence the extent of curl development. In wool it has been noted that stretching while wet and then exposure to bond severing conditions, such as steam, leads to super contraction. Perhaps an analogous situation exists in some feather treating operations when softening agents and other chemicals together with the feather picking operation induce a greater extent of curl development upon drying. Actually there is some limited data to indicate that wet picking is more desirable in producing higher curl development than ordinary dry plucking. Some evidence has also been obtained to suggest that a picker-type- or drawing-action on wet feathers increases curl development over that achieved by normal straight chemical treatment.

In general then, the speculation that swelling and contraction or the swelling, stretching, and contraction are significant conditions for curl development appears to be confirmed.

Obviously unless a curled chicken feather particle remains curled and continues to behave in its three-dimensional form, little over-all

benefit will be gained bulkwise. The curled feather, therefore, must be fixed so as to remain curled whether exposed to a damp or dry atmosphere and after having been subjected to moderately high compressive stresses.

A number of methods have been considered for this fixation of the curled structure after the operation of high bulk form alteration. For practical reasons, of course, non-aqueous systems had to be avoided. This restriction made necessary emphasis upon water solutions, emulsions or dispersions of cross-linking agents and those reagents suitable for use under conventional, commercial conditions. Drastic changes in the cystine linkages were not believed desirable if excessive brittleness was to be avoided. Actually, alteration of these bonds in themselves would not be expected to offer the stability needed. A controlled alkali treatment using tri-sodium phosphate was found to allow for improved curl development and the function of such a treatment seems to be that of increasing swelling without causing excessive damage at the cystine bond. If we examine a somewhat modified picture of the curled molecule, it will be noted that three main bridges are available and these would determine the stability of the protein. When all bridges are intact, the structure is quite resistant to deformation. Opening of both the inner salt linkages, which is quite easily accomplished above or below the isoelectric point, would also allow the main backbone structure to twist, compress or elongate. As long as these inner salt bridges are free to open and water can enter into the structure and cause plasticization, form-stability and water resistance cannot be achieved. We are told that the spacing of the inner salt bridge in wool increases from 9.8 angstroms to 10.8 angstroms upon wetting, and if we assume that chicken feather keratin is of a similar nature, this would explain why these feathers become soft and swell in water. To avoid water penetration, then, it would seem necessary to attempt to eliminate insofar as possible the polar characteristics of the fiber. Several methods have been used to accomplish this transformation of feathers by reaction with the carboxyl and amine groups. In the previous paper presented by Dr. Florio describing the alum process, the reaction presumably is effective because of the tie-up with the carboxyl groups. A reaction with the amine groups is accomplished in leather tanning and in wool modification. Unfortunately, one of the most common reagents employed in both treatments, formaldehyde, has not produced suitable curled stabilized chicken feathers although applications under various conditions were tried out. Attention, therefore, in our laboratory was directed toward various other curling reagents, especially to the more reactive dialdehydes. From these investigations it was found that glyoxal possessed fixative properties and, in addition, a means for accomplishing other end requirements. The glyoxal reaction with chicken feathers was found to progress rapidly over a wide range of the pH scale. Indications from numerous treatments applied suggest that optimum penetration occurs at lower pH in the range of 2 to 3 and that more sur-

face reaction, apparently, takes place near the neutral point. Accordingly, most of the treatments with glyoxal have been applied to chicken feathers at pH between 2 and 3 using aluminum sulfate for bringing down the pH of the commercial glyoxal. Reaction of chicken feather keratin and glyoxal produces a stabilized bond and allows for curl fixation. Curled feathers so processed remain curled when exposed to 100% humidity at 100° F. and are resistant to microorganism attack. If these feathers are held flat, for example, while exposed to 100% humidity at moderate temperature, or even if held flat between moistened blotting paper and then heated to 200° F., the curled form returns after removal of the restraining force.

Compared with waterfowl feathers in the common odor development test, wherein samples are exposed to 100% humidity at 100° F., glyoxal treated feathers have developed no odor, even after three weeks, while waterfowl feathers invariably become significantly odoriferous after five days. A very outstanding improvement is noted in bulk properties—the first and most important requirement of any insulation material. With a suitable raw material the bulk filling power values are equal to or higher than those recorded for waterfowl feathers. Laboratory samples invariably measure over 5 cm. and sometimes as high as 6 cm. filling power as compared to the value of 5.5 cm. for the better waterfowl feathers. Even waterfowl feathers have been upgraded from a filling power of less than 4.5 cm. to over 6 cm. by the process. These represent the results obtained from normal experience in feather treatment by the glyoxal process in the laboratory. Similar results have not been obtained in commercial trial operations with the same chemicals. The reasons for these discrepancies will be considered somewhat later.

Before proceeding into the details of the glyoxal processing technique, mention should be made of finishes applied to chicken feathers. In general, mere surface finishing has not been found to offer adequate fixation of curl or water repellency. Some protective films have improved the curl retention, but perhaps the most significant influence of special finishes has been their ability to confer antilubricity to feathers and thereby improve bulk filling power qualities. Surface finishes usually of wax dispersions containing less than 0.2% of a hydrophobed silica gel, have increased the filling power of commercially "curled" or crushed chicken feathers from about 3 cm. to well over 6 cm. filling power. These findings seem to suggest the similarity between surface lubricity as accomplished through the hydrophobed silica gel and the resisting influence of the nodules on waterfowl feather barbules. Unfortunately, while the latter serve to prevent particles from intermeshing easily and are quite specific in this action, the anti-lubricating finish as applied through the silica gel process inhibits particles from coming together under mild conditions of agitation, but once the fibers come together through excessive wear, they are very difficult to separate and actually tend to felt together under these conditions. They rarely can be refluffed to any appreci-

able degree. Surface finishes, in addition, have not been satisfactory for promoting significant improvement in the water repellency of chicken feathers. Some improvement in stiffening can be accomplished, but surface finishing techniques are quite inferior to a glyoxal tanning technique.

In any chemical treatment certain optimum conditions must be maintained for optimum results. In feather processing additional limitations exist since the raw material is so varied. It will be recalled that we inferred that perhaps curling of chicken feathers did occur by conventional processing techniques, but that we ordinarily would not recognize the modifications because no stabilizing process had been applied. It was this feature that the glyoxal process has given us if nothing else. It has permitted us to differentiate between feather types and indicate the influence of various type feathers on bulk improvement properties.

The feathers from immature chickens in the age group of eight to twelve weeks have provided higher bulk properties by the normal glyoxal treatment than those from much older birds. In addition, the feathers from certain breeds of chickens seem to process more satisfactorily to provide high bulk filling power. Feathers from certain type cross-breeds, for those feather types studied, have invariably been more suitable than other more common feathers. For instance the Indian River, Silver Hamp and Delaware Cross breeds of chickens have provided a raw material that was more satisfactorily upgraded than those feathers from such birds as the Plymouth Rock, White Rock, Rhode Island Red and New Hampshire Red in about that order. Among any given type of feathers there again is some preference to be indicated. Obviously the large tail and wing feathers must be ex-included. Then too, those feathers that contain an appreciable amount of fluff seem to resist curling, or at least offer little bulking value when curled because of their extreme softness. In general the small vaned feathers are better raw materials to provide a high bulk filler by the glyoxal process. Obviously, then, selection of the feathers would seem desirable. In the laboratory, using immature feathers from Indian River birds, we have recorded filling power values repeatedly in the order of 5.5 cm. filling power.

As noted there are some indications that the plucking conditions influence subsequent curl development. Feathers obtained by the dry plucking technique appear to be more resistant to curling even in the immature types than the wet plucked feathers. Fortunately wet plucking is a common feather removal technique. Conventional practice in the wet plucking operation calls for soaking the bird in a solution of wetting agent or a water softener at 128 to 130° F. for one and one-half to three minutes depending upon the age of the bird. Plucking is usually accomplished as the fowl are carried through machines in which rubber fingers withdraw the feathers and sometimes there is specific equipment for removing the feathers from certain areas of the bird.

Since chicken feathers are more easily wetted than waterfowl feathers because of a more effective surface protective film on the latter, contamination with blood is more common in the chicken feather product. Actually during the study of surface finishes and investigations of methods for achieving suitable penetration of additives, the difficulties in removing coagulated blood and surface finishes was recognized as quite a problem. Various cleansing systems were studied. It wasn't until a satisfactory blood-solubilizing chemical was included with, or used prior to, a cleansing operation that it was possible to reduce the natural finish on chicken feathers significantly by any laundering technique. Further studies with detergent systems with and without blood-solubilizing pretreatments and compared also with dry cleaning operations indicate there are advantages for using the blood-solubilizing agent and non-ionic detergent cleansing methods. Accordingly, the recommendations that we would make for any cleansing process would be to include both the blood-solubilizing additive and a non-ionic detergent cleansing media preferably at a temperature of 110 to 125° F.

A curl in the quill of a chicken feather can be accomplished rather easily especially if feathers from immature birds are employed. To induce feather curling or to cause curl to form in the more-difficult-to-soften feathers of other types or breeds, a pretreating operation has been found to be effective. This involves processing after laundering and wringing, but without rinsing, in a 1% solution of tri-sodium phosphate for perhaps as long as 30 minutes at about 110 to 120° F. The conditions are critical only to the extent that mature feathers resist softening more than do immature feathers and the character of the agitation will determine the optimum duration and temperature of the treatment. Wring, and rinse thoroughly to remove TSP.

Although glyoxal concentrations over a rather wide range have been applied to feathers, the 1% solution has been used most extensively and provides satisfactory results. A feather to solution weight ratio of one to two pounds of feathers to 40 pounds of solution has been common laboratory practice. Since the hydrogen ion concentrations seem to determine the extent of penetration, a pH on the order of 2 to 3 has been maintained through the use of 0.1% aluminum sulfate (iron free). The recommended temperature of processing may be given as 100 to 120° F. for thirty minutes depending again upon the type of agitation applied. When the feathers have been satisfactorily processed they may be stored in the wet state for as long as several weeks. No degradation appears in glyoxal-treated feathers even when wet. Such resistance to disintegration would not be common with wet, untreated chicken feathers or waterfowl feathers. Only after drying is the significant yellow tinge in the feather detected and this serves to indicate that reaction has proceeded.

For optimum curl development the drying operation is most critical. According to laboratory experience and the curl development hypothesis already mentioned, curling only occurs because of the con-

traction that takes place during the drying operation. Furthermore, unless the curled feathers are removed from the moist atmosphere they may again be plasticized before the curing condition takes place. These dried, but uncured, curled feathers can be straightened in the presence of moisture and this, therefore, represents one of the most critical operations in the glyoxal, or for that matter in the alum processing operations. For best results the dried feathers must be removed from the drying chamber to avoid exposure to moisture prior to cure. The ideal process would seem to involve carrying the mostly dry, light and fluffy feathers away from the wet mass into a region such as to a conveyor belt where relaxation drying could be completed and subsequent curing at 180 to 200° F. could be applied.

In the course of discussion of the glyoxal treatment of chicken feathers restricting conditions were mentioned. Starting from the beginning of the process we can list several critical operations in their order of application. First, a suitable raw material should be selected for optimum results. Current information suggests that certain feathers, especially the small vaned feathers of immature birds of certain cross-breeds are most satisfactory. Second, plucking conditions should be understood and altered if desirable to allow optimum results. Separation of large feathers at this point eliminates dust problems in subsequent operations. Third, blood-solubilizing and cleaning agents should apparently be included although such treatments are not necessarily critical in promoting curl formation and curl fixing. Fourth, pretreating conditions are selected on the basis of the type of feather being processed and the mechanism of the action applied. A 1% tri-sodium phosphate solution may be used in any treatment providing the severity of processing is controlled by limiting temperature and mechanical action. Fifth, glyoxal processing must be conducted in iron-free equipment and at 1% concentration with iron-free chemicals. In the laboratory where an Easy Washing Machine was the type of equipment used, the reaction was carried out for 30 minutes at a temperature of 110 to 120° F. Higher temperatures and excessive agitation led to breakdown of the feathers. Sixth, drying is probably one of the most critical operations. Complete relaxation of the feathers must be allowed as they dry and moisture must be removed without coming in contact with the previously dried product. Seventh, curing may be accomplished by aging at room temperature although accelerated curing at 180 or 200° F. for 5 to 10 minutes seems to provide a somewhat superior product. Eighth, fractionation certainly must follow glyoxal processing just as this operation is necessary in waterfowl feather operations. The elimination of large feathers in the plucking operations serves to eliminate dusting and offers overall processing advantages.

Now that the curled chicken feather has been prepared in the laboratory, just how well does this product compare with the waterfowl material according to the requirements previously listed? Suppose,

then, we reconsider the requirements previously mentioned and compare the properties of this new product with waterfowl materials.

There is no reason to dispute the similar insulation qualities of curled chicken feathers and waterfowl feathers if bulk properties are equivalent. Experience indicates that, according to filling power data, curled chicken feathers, prepared by the glyoxal process, are at least equivalent bulk-wise to the waterfowl feathers. On the basis of bulk properties, under static conditions, then, the modified chicken feathers are essentially equivalent to waterfowl feathers.

Relatively crude laboratory tests indicate that the memory of curled chicken feathers processed by the glyoxal technique is quite good. The curled form returns to the quill of these modified products after they have been removed from a restraining force under moist, warm conditions. The high bulk form returns even after the feathers have been held straight between wetted blotting paper at 200° F. Again under static conditions of testing the characteristics of the new high bulk form appear to be satisfactory.

Since the new filler, the glyoxal modified chicken feathers, so closely resemble waterfowl feather in that they are individual, discrete particles, they would seem to offer drape qualities. Actually, samples of glyoxal treated Indian River Feathers not only behave like waterfowl feathers but feel much like waterfowl feathers in that they lack the harshness so common in conventional chicken feathers.

Again the similarity of the treated chicken feathers and waterfowl feathers suggests comparable resiliency and compression resistance. No detectable embrittlement has been observed in the treated chicken feathers even after several months' storage. Little variation on this basis would be expected.

One of the more striking observations in comparing untreated chicken feathers with glyoxal treated chicken feathers is the outstanding water repellency of the modified material. If we dip the treated feathers in water, no wetting occurs and the water is collected on the surface as spherical droplets.

The glyoxal treatment of feathers does not increase flammability, therefore the product is acceptable in this respect.

Very little data, unfortunately, is available relating bulk properties of glyoxal treated feathers with resistance to actual or simulated wear. A limited number of laboratory studies have been conducted comparing bulk properties of waterfowl and treated chicken feathers after exposure to the simulated wear that is provided by one of our machines. These studies have indicated that suitably treated samples resist degradation just about as well as do waterfowl feathers. Similarly, the laundering tests have not been discouraging although very little data has been obtained. Perhaps most significant in these tests is the observation that the laundering of these glyoxal treated chicken feathers, even when enclosed in pads, has no deleterious effects on bulk properties. Again it must be cautioned that very little data is

available on this or any other of the durability aspects to indicate conclusively the permanency of the curl in modified chicken feathers.

Since the primary reason for conducting a study on chicken feathers was to substitute these by-products of the American poultry industry for waterfowl feathers, there is little question regarding their extensive availability. Actually, considerable quantities of all chicken feathers are domestically available and the only real concern is whether a suitable quantity of the preferred types will be offered. Current trends in poultry production are toward the use of younger birds as fryers and broilers and to an increased demand for white and white cross-type birds. These are favorable signs. Cost-wise the raw material is in a favorable position and chemical charges do not seem to indicate any severe change in this condition. In addition to the comparative features mentioned it should be noted that glyoxal treated chicken feathers resist microorganism attacks even better than waterfowl feathers. The normal odor test, as previously mentioned, causes no odor formation in glyoxal treated feathers even after several weeks' exposure, whereas significant odor develops in waterfowl feathers after five days.

The overall picture for chemically modified chicken feathers as outlined from laboratory studies is especially favorable. The most important and significant problem today is the conversion of the laboratory results into commercial reality. This translation is not so simple as we have already learned. None of the several plant trials has provided reasons for optimism, but neither have conditions been suitable. Further efforts are being made and current plans suggest more suitable arrangements.

Before closing the subject of glyoxal treatment, mention might be made of some other features offered by this process. It will be recalled that it was necessary to limit the glyoxal processing temperature. Investigations have shown that when whole feathers are exposed to the glyoxal reaction, at considerably higher temperatures than that of the 120° F. mentioned, let us say in the order of 180° F., a feather fiber type product results. This material would seem to be of value in uses assigned to feather fibers because, in addition to having a fiber-type form, it is water repellent, is resistant to microorganisms and possesses at least the bulking value of ordinary chicken feather fibers.

The use of other dialdehydes including gluteraldehyde and alpha hydroxyadipaldehyde offers certain advantages in feather processing. Apparently results similar to those obtained by glyoxal can be achieved. One advantage offered by these reagents is their potentially lower cost when compared with glyoxal. In addition, rather unusual surface conditions seem to be provided by alpha hydroxyadipaldehyde. In very limited studies feather fibers so processed have been upgraded bulk-wise whereas other techniques have failed to improve the bulk properties of feather fibers.

These remarks should indicate above all that a number of problems remain in using chicken feathers as replacements for waterfowl mate-

rials. The plans now formulated to conduct pilot plant studies should provide some answers that have not yet been obtainable. Above all it should be recognized that we have an entirely different type of treatment being applied to chicken feathers in this and the previously discussed process than normally applied in feathers. Such marked deviations from common practice require special handling and processing conditions that are not currently available in the feather treating trade.

In the few minutes remaining mention may be made of an entirely different type of feather filler that seems worthy of further consideration. In our early work, while we had recognized the importance of the curled form for improvement of bulk properties, a method was developed for substituting a synthetic quill, together with chicken feathers to provide a high bulk filler. In this process a monofilament of nylon or preferably of Dacron at 5 to 20 mil diameter was formed into a helix. The curled helix then was passed through an adhesive, the adhesive-covered filament was subjected to an atmosphere of feathers or feather-fiber particles and the product was then dried. The end result was a spring-like material covered with a soft, feathery or feather fiber coating. Among some one hundred and thirty samples of these preparations, 93% have provided a filling power of over 4 cm., 75% of over 4.5 cm. and 36% of over 5 cm. None of the feathers used in these early products were treated with glyoxal and most of the materials were made with a nylon monofilament so that somewhat better results might be expected using an improved feather on the preferred Dacron filament sustaining form. Some trials have been made on the fillers as used in sleeping bags and there is no reason to believe at this time that such a filler would not provide rather substantial insulation properties.

The primary objection to this last process was the difficulty anticipated in specifying the product. This might occur; in any case, the process and the potentials that exist in the method are mentioned here as another method for achieving high bulk insulating properties from a chicken feather raw material.

APPENDIX[1]

G. Feather Processing

In order to establish the most satisfactory and practical conditions for upgrading chicken feathers, every limiting feature of the raw material, the process and the treating facilities must be considered. Experience has shown that many factors influence the treatments and have a direct effect on resultant bulk properties. Thus the various feathers from any given bird, the feathers from different types of

[1] From "Final Report of Garment Filling Materials Fellowship No. 2 (January 3, 1951, through March 31, 1954), Quartermaster Corps, Department of the Army, Contract No. DA44-109 qm-385."

birds, the age of the birds which provide the raw material, the pre-treating conditions of handling, and the processing equipment and conditions have a marked effect upon the bulk properties of the modified feathers.

1. THE INFLUENCE OF FEATHER TYPES

The chemical (glyoxal) treatment of various types of chicken feathers has firmly established that the feathers from certain cross-breed immature chickens provide a most significantly high bulk (6+ cm. filling power) filler if the product is adequately processed and fractionated. Glyoxal-treated feathers from immature Indian River, Silver Hamp and Delaware Cross chickens, invariably contain a higher percentage of curled particles than similarly treated immature feathers from such common breeds as the New Hampshire, Rhode Island and White Rock. The filling power values recorded for treated and fractionated samples of the better feather types are usually between 5.5 and 6+ cm., whereas the filling power values for treated and fractionated samples of the inferior types of feathers rarely exceed 5 cm. (Table X).

A visual comparison of the two groups of feathers has indicated several variations that may serve to explain these observations. The most obvious difference is the apparently greater percentage of high fluff feathers in the red—as compared with those in the white—or white cross-feathers and the inability of these high fluff (above ½ fluff[19] feathers to curl pronouncedly. The fluff is so soft that it would hardly offer any bulk support even if the quill were bent. While differences in quill cross-section do occur, perhaps the relative stiffness of the quill and the ratio of weights of quills to barbs are more important factors in determining bulk properties. The cross-breed feathers seem to be stiffer than the inferior bulk producing red- or white-feathers and also seem to possess a lower quill to barb weight ratio. Thus, the mostly vaned, thin quill but reasonably stiff feathers, when stabilized in the curled form, may be expected to yield products with filling power values of at least 6 cm. Any deviation from so high a bulk value is attributable to dilution with fluff[19], relatively soft, high weight ratio quill to barb feathers and/or poor stabilizing treatment.

2. THE INFLUENCE OF FEATHER MATURITY

Mature feathers have been shown to resist curling by simple glyoxal processing, apparently because of greater natural stability. Actually, mature feathers have been curled by moderate pre-treatment with such alkaline reagents as tri-sodium phosphate that are believed to alter the stability by modification of cystine linkages in the keratin. By this treatment, mature Plymouth Rock feathers have been curled and by glyoxal processing, the curl has been fixed to provide fractions with filling power values ranging from 3.6 to 5.3 cm. (Table IX). Again, the predominance of high fluff feathers in these mature materials limits bulk improvement.

Table IX

Bulk Improvement (Curl and Curl Stabilization) of Straight Chicken Feathers

Identification	Feather Type	Treatment	Filling Power (cm) [c][1]	Filling Power (cm) [c] [w][2]
M-92	Mixture Collected by P.Q.D., Straight (6 ½ fraction)	Laundered, Glim	2.2	..
N-24	" " " " " "	Agitated hot (120°F.), carefully dried	5.0	..
N-26	" " " " " "	Laundered (0.36% residual finish) + wax-Silica Gel[3]	7.9	..
N-41	" " " " " "	" (0.37% " ") + wax-Silica Gel[3]	5.8	5.6
N-43	" " " " " "	" " " " " "	7.4	6.6
N-44a	" " " " " "	,Sterox, warm (109°F.) 30 minutes carefully dried	5.0	4.6
N-44b	" " " " " "	" " " " 60 minutes carefully dried	4.7	4.7
N-44c	" " " " " "	" " " " 180 minutes carefully dried	3.7	3.7
N-48	" " " " " "	" ,Tergitol, warm + wax-Silica Gel[3]	5.8	5.4
N-61b	Northern, Plymouth Rock, Straight mature	Laundered	3.9	3.2
N-61a	" " " " "	" + wax-Silica Gel[3] blown	6.3	5.6
N-63a	" " " " "	" " " "	6.0	6.0
N-63b	" " " " "	" " " " picked	5.7	5.2
N-64a	" " " " "	" " " " not picked	6.2	4.8
N-64b	" " " " "	" " " " picked	..	5.9
N-85a	" " " " "	.....+ 1.5% add-on Hycar 1502 cold solution	3.1	3.1
Q-20a	" " " " "	0.013% NaSH. 120°F., 15 min. + 1% Glyoxal, 0.1% CrF_3, 120° F., 15 min.	4.0	4.0
Q-20b	" " " " "	Q-20a + wax-Silica Gel[3]	4.8	4.6
Q-25a	" " " " "	1% Na_3PO_4 Soln. 125°F., 30 minutes	4.5	4.1
Q-25b	" " " " " light fraction	Q-25a + 1% Glyoxal, 0.1% CrF_3.FD.[4]OC[5]	5.1	5.1
Q-25c	" " " " " med. fraction	" " " " FD[4].FC[6]	4.2	4.2
Q-26a-1	" " " " " light fraction	1% $Na_3PO_4 \cdot 12H_2O$ Soln., 115°F., 30 min. + 1% Glyoxal, 0.1% CrF_3 (not rinsed) FD,[4] OC[5]	5.1	5.1
Q-26a-2	" " " " " med. fraction	Q-26a-1. FD.[4] FC[6]	3.6	3.6
Q-26b-1	" " " " " light fraction	1% $Na_3PO_4 \cdot 12H_2O$ Soln., 115°F., 30 min. + 1% Glyoxal, 0.1% CrF_3 (rinsed) FD.[4] OC[5]	5.3	5.1
Q-26b-2	" " " " " med. fraction	Q-26b-1, FD.[4] FC[6]	4.4	4.2
Q-30	" " " "	1% Na_3PO_4 Soln., 115°F., 30 min. + 1% Glyoxal, 0.1% CrF_3 FD[4].FC[6]	4.9	5.0
Q-27a-1	Butler Co-op, I.R.[7] Immature straight light fraction	Haemo-Sol. Soak + Laundered + 1% $Na_3PO_4 \cdot 12\ H_2O$ soln., 115°F., 30 minutes + 1% Glyoxal, 0.1% CrF_3, 115°F., 30 minutes FD[4],OC[5]	5.8	5.6
Q-27a-2	" " " " " medium fraction	Q-27a-1. F.D.[4] OC[5]	5.1	5.0
Q-27b-1	" " " " " light fraction	Haemo-Sol. Soak + 1% $Na_3PO_4 \cdot 12\ H_2O$ in launder + 1% Glyoxal, 0.1% CrF_3, 115°F., 30 minutes FD[4], OC[5]	5.5	5.5
Q-27b-2	" " " " " medium fraction	Q-27b-1, FD[4], OC[5]	5.3	5.4
Q-30	" " " " "			
Q-81	DM, I.R., Immature straight	Haemo-Sol. Soak + Launder + 1% $Na_3PO_4 \cdot 12\ H_2O$ + 1% a hydroxy adipaldehyde, 0.2% $Al_2(SO_4)_3 \cdot 18\ H_2O$, 115°F., TD[7]	5.9	..

1. Standard Sinski Filling Power Test
2. Standard Sinski Filling Power Test after moistening filling power tube
3. Hydrophobed Santocel (dimethyl dichlorosilane treated low density silica gel) dispersed in wax emulsion.
4. Fluffer dried. 150-180°F.
5. Oven cured, 200-220°F.
6. Fluffer cured, 180°F.
7. Tumble Dryer, 150-180°F.

Table X

Glyoxal Stabilization of Curled Feathers and Effect of Treating Conditions on Filling Power

Identification	Feather Type	Treatment		Filling Power (cm) [c][1]	Filling Power (cm) [c] [w][2]
P-93a	Chicken Feathers, DM(Y)(Leg + NH),* immature Sample A	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, rinsed twice, 115°F., *Fe Tank*	OD,[3]OC[4]	4.9	5.0
P-93b	Chicken Feathers, DM(Y)(Leg + NH),* immature Sample B	Same treatment and conditions	OD,[3]OC[4]	4.9	4.9
P-93c	Chicken Feathers, DM(Y)(Leg + NH),* immature Sample C	Same treatment and conditions	OD,[3]OC[4]	4.6	4.7
P-93d	Chicken Feathers, DM(Y)(Leg + NH),* immature Sample D	Same treatment and conditions	OD,[3]OC[4]	4.5	4.4
P-93e	Chicken Feathers, DM(Y)(Leg + NH),* immature Sample E	Same treatment and conditions	OD,[3]OC[4]	5.0	5.0
P-93f	Chicken Feathers, DM(Y)(Leg + NH),* immature Sample F	Same treatment and conditions	OD,[5]OC[4]	4.9	4.9
P-93g	Chicken Feathers, DM(Y)(Leg + NH),* immature Sample G	Same treatment and conditions	FD,[5]AC[6]	5.0	4.9
P-93h	Chicken Feathers, DM(Y)(Leg + NH),* immature Sample H	Same treatment and conditions	FD,[5]FC[7]	4.2	4.1
P-94a	Chicken Feathers, DM(Y)(Leg + NH),* immature	Retreatment of Uncured P-93	FD,[5]OC[4]	5.2	5.4
P-94b	Chicken Feathers, DM(Y)(Leg + NH),* immature	Same treatment and conditions	FD,[5]OC[4]	4.8	5.0
P-94c	Chicken Feathers, DM(Y)(Leg + NH),* immature	Same treatment and conditions	FD,[5]OC[4]	4.5	4.4
P-96	Chicken Feathers,Ro(AA) (CoR)	Same treatment and conditions	FD,[5]FC[7]	3.0	..
P-99a-1	Chicken Feathers,DM(CC)(WR + NH),* immature Sample A *light fraction*	Same treatment and conditions	FD,[5]OC[4]	5.0	5.0
P-99a-2	Chicken Feathers,DM(CC)(WR + NH),* immature *light fraction*	Same treatment and conditions	FD,[5]OC[4]	5.7	5.8
P-99a-3	Chicken Feathers,DM(CC)(WR + NH),* immature *med. fraction*	Same treatment and conditions	FD,[5]OC[4]	4.8	5.0
P-99a-4	Chicken Feathers,DM(CC)(WR + NH),* immature *med. fraction*	Same treatment and conditions	FD,[5]OC[4]	4.2	4.2
P-99b-1	Chicken Feathers,DM(CC)(WR + NH),* immature *light fraction*	Same treatment and conditions	FD,[5]OC[4]	5.9	6.0
P-99b-2	Chicken Feathers,DM(CC)(WR + NH),* immature *med. fraction*	Same treatment and conditions	FD,[5]OC[4]	5.0	5.1
P-99b-3	Chicken Feathers,DM(CC)(WR + NH),* immature *med. fraction*	Same treatment and conditions	FD,[5]OC[4]	4.5	4.5
P-99b-4	Chicken Feathers,DM(CC)(WR + NH),* immature *med. fraction*	Same treatment and conditions	FD,[5]OC[4]	4.7	4.6
P-100a	Chicken Feathers,Ro(BB)(NH),* immature Sample A	Same treatment and conditions	FD,[5]FC[7]	3.4	..
P-100b	Chicken Feathers,Ro(BB)(NH),* immature Sample B	*$MgSiF_6$* for $Al_2(SO_4)_3$ otherwise same conditions	FD,[5]FC[7]	2.1	..
P-90a-1	Chicken Feathers,DM(X)(IR),* immature many large feathers *light fraction*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, *90°F.* rinsed well *Al tank*	FD,[3]OC[4]	4.4	4.4
P-90b-2	Chicken Feathers,DM(X)(IR),* immature *light fraction*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, *110°F.* rinsed well *Al tank*	FD,[5]OC[4]	5.6	5.6
P-90c-3	Chicken Feathers,DM(X)(IR),* immature *light fraction*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, *125°F.* rinsed well *Al tank*	FD,[5]OC[4]	5.6	5.4

Table X (continued)

Identification	Feather Type	Treatment		Filling Power (cm) [c][1]	Filling Power (cm) [c]	Filling Power (cm) [w][2]
P-90a-2	Chicken Feathers,DM(X)(IR),* immature *heavy fraction*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, *90°F.* rinsed well *Al tank*	FD,[5]OC[4]	4.0	4.0	
P-90b-2a	Chicken Feathers,DM(X)(IR),* immature *heavy fraction*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, *110°F.* rinsed well *Al tank*	FD,[5]OC[4]	4.3	4.4	
P-90c-2	Chicken Feathers,DM(X)(IR),* immature *heavy fraction*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, *125°F.* rinsed well *Al tank*	FD,[5]OC[4]	3.4	3.5	
P-85a	Chicken Feathers,DM(T)(WR),* immature *light fraction*	Same treatment 110°F. rinsed well *Al tank*	FD,[5]FC[7]	5.8	5.7	
P-85b	Chicken Feathers,DM(T)(WR),* immature *light fraction*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, 110°F. rinsed well	FD,[5]OC[250°]	5.1	5.1	
P-85c	Chicken Feathers,DM(T)(WR),* immature *light fraction*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, 110°F. rinsed well [Glyoxal Soln—*pH adjusted to 7.6*]	FD,[5]FC[7]	5.6	5.8	
P-91a	Chicken Feathers,DM(X)(IR),* immature *no fraction*	Same treatment and conditions [Glyoxal Soln—*pH adjusted to 7.6*]	FD,[5]OC[4]	4.2	4.2	
P-91b	Chicken Feathers,DM(X)(IR),* immature *no fraction*	Same treatment and conditions	FD,[5]FC[7]	3.6	3.5	
P-97a	Chicken Feathers,Ro(BB)(NH),* immature many large feathers	Haemo-Sol, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, 110°F. *FeTank*	FD,[5]OC[4]	4.5	4.4	
P-97b	Chicken Feathers,Ro(BB)(NH),* immature many large feathers	Same treatment and conditions	FD,[5]FC[7]	3.2	(not sat. relaxed)	
P-97c-1	Chicken Feathers,Ro(BB)(NH),* immature *part fract.*	Same treatment and conditions	FD,[5]FC[7]	4.3 (Cure 170°F. —2 min.)	4.3	
P-97c-2	Chicken Feathers,Ro(BB)(NH),* immature *part fract.*	Same treatment and conditions	FD,[5]FC[7]	5.6 (Cure 186°F. —7 min.)	5.7	
P-97c-3	Chicken Feathers,Ro(BB)(NH),* immature *part fract.*	Same treatment and conditions	FD,[5]FC[7]	5.2 (Cure 190°F. —15 min.)	5.2	
P-97c-4	Chicken Feathers,Ro(BB)(NH),* immature *part fract.*	Same treatment and conditions	FD,[5]FC[7]	5.4 (Cure 190°F. —25 min.)	5.5	
P-95-a	Turkey Feathers, DM(Z)(Beltz),* immature *part fract.*	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, 115°F. rinsed well *Al Tank*	FD,[5]FC[7]	5.3	5.3	
Q-68a	Goose Feathers,P.Q.D. as received			3.9	..	
Q-68b	Goose Feathers,P.Q.D. as received	MXP wash, 1% Glyoxal, 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$ 110°F. rinsed well *Al Tank*	FD,[5]FC[7]	6.6	..	

Table X (continued)

Identification	Feather Type	Treatment			Filling Power (cm) [c][1]	Filling Power (cm) [c] [w][2]
Q-69a	Chicken Feathers,DM(OOO)(IR),* immature	Haemo-Sol Soak, MXP wash, 1% Glyoxal + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, 110°F. rinsed well	*Al tank*	FD,[5]FC[7]	4.4	..
Q-69b	Chicken Feathers,DM(OOO)(IR),* immature	Same treatment and conditions	*Cu Tank*	FD,[5]FC[7]	4.3	..
Q-53a	Chicken Feathers,BCo(FFF)(NH + WR),* immature *light fraction*	Haemo-Sol, 1% $Na_3PO_4 \cdot 12H_2O$. + 1% Glyoxal (wash wheel)[8] 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, 105°F. rinse well		TD,[9]OD[4(250°)]	4.7	..
Q-53b	Chicken Feathers,BCo(FFF)(NH + WR),* immature *light fraction*	Same treatment and conditions		TD,[9]AC[6]	5.5	..
Q-55a	Chicken Feathers, S (GGG)(NH + WR),* immature *no fraction*	Same treatment and conditions	wash wheel[8]	TD[9]	4.6	..
Q-55b	Chicken Feathers, S (GGG)(NH + WR),* immature *no fraction*	Same treatment and conditions	*Al Tank*	TD[9]	4.7	..

1. Standard Sinski Filling Power Test
2. Wetted Wall Filling Power Test
3. Oven dried—220°F.
4. Oven cured—220°F., 10-20 minutes
5. Fluffer dried—180°F.
6. Air Cured—75-80°F.
7. Fluffer Cured—180°F., 15-20 minutes
8. Commercial 300# (wet clothes) capacity wash wheel—feathers retained in orlon bags.
9. Tumble dried (electric home dryer) up to 180°F.

* Feather supplier, type and conditions
DM = Dick's Market (Fresh Supply)
Leg = Leghorn
NH = New Hampshire
WH = White Rock
CoR = Columbia River
Ro = Roseport Altoona (not fresh supply), wing and tail feathers included
BCo = Butler Coop (fresh Supply)
IR = Indian River
Beltz = Beltzville White
S = Saebacker (fresh supply)

From the above comments, it would appear necessary to arrange a treating schedule on chicken feathers according to whether the raw material is from mature or immature birds. The only really critical phases are those involving the phosphate and glyoxal treatments. The use of the phosphate treatment on immature feathers is not absolutely necessary but has been advantageous for increasing the yield of curled product from these feathers. When immature feathers are so treated, care must be exercised to control the concentration, the temperature and the time of contact between the feathers and phosphate solution in any given type of mechanical agitator. Excessively severe conditions must be avoided to prevent feather degradation as may be evidenced by the production of fly and barb fibers. The conditions for the alkaline phosphate treatment of mature feathers are not so critical and one percent concentrations of tri-sodium phosphate have been applied at 120° F. for 60 minutes without degrading effects to produce a significant curl when processed in an Easy Washing Machine. Under similar conditions of mechanical agitation, immature feathers must be processed less drastically, for example, with a solution containing one-half percent phosphate for perhaps a maximum of 30 minutes at about 110° F. Unfortunately these same conditions do not apply to the processing of the mature or immature feathers in equipment of different mechanical activity.

In the glyoxal reaction, the conditions are not so critical and moderate variations in concentrations, temperature and time have little or no influence on the stabilizing effectiveness of the reagent. Only when excessively high temperatures are employed (160-180° F.) does the glyoxal treatment exert a reducing action so severe as to cause disintegration and fiber production.

[See references 36, 37, 38, 39, 40, 41]

3. Pretreatment Operations

Both dry and wet methods are used commercially to remove feathers from fowl. Feathers obtained by the dry plucking operations appear to be more resistant to curling, even in the immature types, than wet plucked feathers. Wet feather removal methods are undoubtedly the most common in commercial operation and involve a thorough wetting-out process to facilitate feather removal. The soaking is usually facilitated by means of wetting agents and/or water softeners in a solution maintained at 128 to 132° F. Depending upon the age of the birds being processed, the dwell time may extend from 1.5 minutes for young birds to 3 minutes for mature birds. In most plants[20], the birds are carried on a conveyor and drawn through the solution into the mechanical pickers where serated rubber fingers draw out the feathers. Certain types of feather pickers are specific in their action—removing the feathers from one general area of the carcass. Thus, the potential availability in certain plants of feather fractions in the raw, untreated state.

a. *Plucking Conditions and Subsequent Curl Development*

The wet plucking operations as normally carried out in poultry processing plants may have an effect on curl development. The fact that dry plucked feathers usually do not display a curl and the apparent advantages for curl formation as a result of wet stretching, suggests that the wet plucking operation can serve to favor initial curl development in chicken feathers. Unfortunately, it is not easy to confirm this hypothesis under ordinary conditions of processing. While significant numbers of feathers are observed to curl as they dry following the wet plucking operation, this preferred feather form is not suitably permanent to be retained after the conditioning required in the standard filling power test. So it is that many of these effects of pretreatment and of the feathers themselves were not recognized until a method was found to fix the curl for satisfactory evaluation.

4. Blood and Soil Removal

a. *Haemolytic Agents*

During the ordinary poultry processing operation, some blood is transferred to the feathers, especially during the soaking operation. Chicken feathers being more easily wetted than waterfowl feathers, readily pick up the blood from the bath and other regions of the processing operation, where blood may contaminate the feathers. If the wet feathers were immediately processed, perhaps most of this blood could be removed by cold water washing as is attempted in many feather plants. Because warm soak solutions are used and because the feathers are never ideally processed, coagulation of the blood usually occurs to make removal difficult. Experimental cleansing studies have indicated that blood removal is not easily achieved with ordinary detergent systems and that the presence of blood interferes with natural finish- and soil-removal. Furthermore, the presence of blood on chicken feathers is believed to lead to poor resistance to attack by microorganisms and to cause the rapid development of odoriferous products of degradation in the presence of moisture. Thus, to promote natural finish removal and soil elimination and to facilitate subsequent treatment, it is considered advisable to remove all traces of blood. This is particularly important in applying surface finishes to chicken feathers. The presence of even small quantities of blood seems to mask the natural finish and make removal difficult, regardless of whether a solvent or aqueous-detergent cleansing system is employed to effect the elimination of the finish. Both solvent cleansing (commercial drycleaning) and aqueous laundering methods have been studied for effectiveness in reducing natural finish but not until blood solubilizing precleansing operations were employed could the natural finish be appreciably reduced with single applications of such treatments.

[See references 36, 37, 38, 39, 40, 41]

In the laboratory, one haemolytic agent (Haemo-Sol) has been used at 0.06 percent concentration in a heated (125° F.) soak solution, prior to laundering or treatment, for the successful removal of blood from feathers. A list of haemolytic agents and the supplier for each is provided below:

Trade Name	*Company*
Weck Cleaner	Edward Weck & Co., Inc. 135 Johnson St. Brooklyn, N. Y.
Arex	Will Ross, Inc. Milwaukee, Wisc. Cohoes, N. Y.
Dynaklen	American Hospital Supply Corp. Evanston, Illinois
Instru-San	Huntington Laboratories Huntington, Indiana Toronto, Canada
Alconox	Alconox, Inc. 61-63 Cornelison Ave. Jersey City 4, N. J.
Coagusol	Hospital Liquids, Inc. Chicago, Illinois
Haemo-Sol	Polychem Corporation 501 Fifth Avenue New York 17, N. Y.

b. *Detergents*

The cleansing of feathers is most practically carried out by means of an aqueous laundering operation (Table XI). Since some neutral salts affect keratin, and proteins will absorb detergent, care must be exercised in the selection of the cleansing medium. The swelling and contraction influence of certain salts in proteins has been demonstrated. These effects may be used to advantage in promoting curling of feathers and, therefore, need to be studied for this application.

Combinations of ions with proteins involve two types of molecular forces—those of specific attraction and those of electrostatic *coulombic* forces. When an isoelectric protein such as keratin combines with hydrogen ions, it acquires a positive electric charge. The surface of such a protein molecule exhibits a positive electric potential, repulses cations and exerts an attractive force for anions. Adsorption of anions will diminish the positive charge and counteract the effect of the adsorption of hydrogen ions on the electric potential. Thus, the electrical forces between protein and ions depend on the amount and nature of all ions present in the system. Further complications arise

Table XI

Natural Finish Removal and Filling Power

Identification	Feather Type	Treatment	CCl_4 Extractable Residue	Filling Power (cm) [C]
M-26	Chicken Feathers, Globe B crushed "curled"	as rc'd	1.16%	2.9
M-28	Chicken Feathers, Globe B crushed "curled"	Twice dry cleaned[1]	0.31	3.5
M-2	Chicken Feathers, Globe C crushed "curled"	as rc'd	2.16	3.0-3.3
M-6	Chicken Feathers, Globe C crushed "curled"	Once dry cleaned[1]	0.60	3.3
M-21	Chicken Feathers, Globe C crushed "curled"	Twice dry cleaned[1]	0.21	2.9
M-50	Chicken Feathers, Globe C crushed "curled"	Twice dry cleaned[1]	0.42	...
M-87a	Chicken Feathers, Globe C crushed "curled"	Soap Scoured,[2] fresh soln.	0.82	...
M-87b	Chicken Feathers, Globe C crushed "curled"	Soap Scoured,[2] used soln.	1.04	...
M-88	Chicken Feathers, Globe C crushed "curled"	Glim[3] washed	0.64	...
N-6	Chicken Feathers, Globe D crushed "curled"	as rc'd	1.57	...
N-4	Chicken Feathers, Globe D crushed "curled"	Tergitol NPX,[3] washed	0.73	...
N-5	Chicken Feathers, Globe D crushed "curled"	Tergitol NPX,[3] Regal[4] + $Na_4P_2O_7$ washed	0.53	3.2
P-49a	Chicken Feathers, Globe E crushed "curled"	as rc'd	0.69	...
P-49b	Chicken Feathers, Globe E crushed "curled"	Lipase + Haemo-Sol[5] washed	0.64	...
P-49c	Chicken Feathers, Globe E crushed "curled"	P-49b + Monsanto MXP[6] washed	0.33	...
M-23c	Chicken Feather Fibers, Chem. (A)	as rc'd	1.39	3.6
M-27	Chicken Feather Fibers, Chem. (A)	Twice dry cleaned[1]	0.22	4.2
N-45	Chicken Feathers, Straight 6 ½ fract., PQD	as rc'd (plant washed)	0.95	...
N-21	Chicken Feathers, PQD Straight 6 ½ fract.	Tergitol NPX[3], Nacconol[4] & Metso 55[7] washed	0.36	4.3 (temp. curl)
N-40	Chicken Feathers, PQD Straight 6 ½ fract.	Tergitol NPX[3], Nacconol[4] & Metso 55[7] CBS #62 washed	0.37	...
N-44	Chicken Feathers, PQD Straight 6 ½ fract.	Sterox 6 washed	0.42	...
O-25	Chicken Feathers, Northern A, Straight	as rc'd (plant washed)	1.27	...
O-45	Chicken Feathers, Northern A, Straight	Sterox 6 washed	0.47	...
O-54b	Chicken Feathers, Northern A, Straight	Sterox 6 washed	0.61	2.8
O-54a	Chicken Feathers, Northern A, Straight	Sted washed	0.49	2.5
O-54c	Chicken Feathers, Northern A, Straight	Triton X-100, Triton X-45[6] washed	0.71	2.9
O-50	Chicken Feathers, Northern A, Straight	Sterox 6, 2 hr. washed	0.28	...
O-79a	Chicken Feathers, Northern A, Straight	Monsanto MXP[6], 2 hr. washed	0.75	...
O-79b	Chicken Feathers, Northern A, Straight	Monsanto MXP[6], 3 hr. washed	0.66	...
O-72b	Chicken Feathers, DM, Straight (Poultry Proc.)	as rc'd	3.57	...
O-72a	Chicken Feathers, DM, Straight (Poultry Proc.)	as rc'd	2.86	...
O-72d	Chicken Feathers, DM, Straight (Poultry Proc.)	Monsanto MXP[6] 30 min. washed	2.21	...
O-72c	Chicken Feathers, DM, Straight (Poultry Proc.)	Emerel[5] soak	2.57	...
O-72e	Chicken Feathers, DM, Straight (Poultry Proc.)	Emerel soak[5] + Monsanto MXP[6] washed	1.62	...
O-72g	Chicken Feathers, DM, Straight (Poultry Proc.)	O-72e—twice washed	1.49	...
O-72f	Chicken Feathers, DM, Straight (Poultry Proc.)	C.S.S. #62[7] soak + Monsanto MXP[6] washed	0.88	...
O-72h	Chicken Feathers, DM, Straight (Poultry Proc.)	Haemo-sol[5] soak + Monsanto MXP[6] washed	0.51	...
O-76	Chicken Feathers, DM, Straight (Poultry Proc.)	Sted washed	1.07	2.2
O-78	Chicken Feathers, DM, Straight (Poultry Proc.)	Cationic detergent washed	1.12	...
O-61a	Chicken Feathers, L, Buckman B-2 crushed "curled"	Plant rinse + MXP[6] washed	1.20	...
O-61b	Chicken Feathers, L, Buckman B-2 crushed "curled"	O-61a + lab. MXP[6] washed	0.94	...
O-64	Chicken Feathers, L, Buckman B-2 crushed "curled"	O-61a + lab. Sted washed	0.40	3.1

1. Commercial dry cleaning, trichlorethylene solvent
2. Mild soap, wool type scouring operation
3. Non-ionic detergent
4. Anionic detergent
5. Haemolytic (blood solubilizing) agent
6. Built Nonionic
7. Oil & grease solubilizing agent

when the system is not homogeneous but consists of microscopically heterogeneous phases as is the case with the adsorption of ions by insoluble proteins such as fibers. The adsorbed ions penetrate the fibers and may be distributed through the whole cross-section. These ions are accompanied by equivalent amounts of oppositely charged ions and the accumulation of such counter-ions in the second phase is opposed by their kinetic energy which tends to distribute them uniformly in the whole space available. The final adsorption equilibrium is reached when all the forces involved, molecular attraction, electric and osmotic forces, are balanced.

Lundgren et al. [21] have indicated that a dodecyl benzyl sulfonate-egg albumin complex may be formed at suitable concentrations with a composition of three parts by weight protein to one part detergent. Similarly, Putman [22] identified two sodium dodecyl sulphate-serum albumin complexes. The findings suggest further that the combination of anionic detergent and protein is independent of pH between 4.5 and 6.8 involving protein groups, presumably cationic, whose state of ionization does not change with the pH range. Similarly acid titration curves on wool conducted by various investigators suggest that the protein forms dissociated salt-like compounds with anions.

The high intrinsic affinity of surface-active ions for protein requires explanation. We may assume that the surface active ions are absorbed in such a way that their hydrocarbon portion is in contact with the hydrophobic groups of the protein. The ionic groups of the surface active ion may approach the oppositely charged ionic groups of the protein. Whatever the explanation for the observed affinity of surface active agents, especially anionic and cationic types, for protein, it seems apparent that adsorption should be minimized in so far as possible. For this reason, in selecting detergents for feather cleansing attention has been directed especially to the non-ionic detergents, which in addition to their apparently limited tendency for adsorption, are also effective oil and wax (natural finish) solubilizers.

[See references 30, 31, 33, 34, 36, 38, 61, 79]

5. Feather Curling and Curl Stabilization

A curl in the quill of chicken feathers is desirable to improve bulk fill properties and such a curl, we have seen, can be imparted rather easily to the feathers taken from young birds and by the alkali phosphate treatment of mature feathers. But merely curling feathers is not enough, since the normal structure of chicken feathers keratin is such that any other physical form may take place upon plasticization. How then, can a curled feather be made to retain this high bulk form by a process that can be applied simply, practically and economically.

A number of techniques have been used to fix the curled form in chicken feathers. Wax finishes have served to maintain the curl under conditions of standard temperature and humidity to provide filling power values ranging from 3.5 to over 5 cm. (Table IX). Similarly,

resinous additives have been applied to feathers to provide bulk improvement through curl fixations. While these surface treatments and possibly such others as the elastomers have had a kind of stabilizing effect on curled feathers, they were feared to be less permanent in their curl retention features than potentially possible by chemical means. Therefore, a concerted effort was made to apply a chemical modification process that could lead to effective stabilization of a curl in chicken feathers.

Naturally, the similarity between hair, wool and feathers suggested that feathers be given a permanent curl by a technique similar to that used to accomplish this condition in hair. The "permanent" treatments used in hair depend generally upon the opening and reformation of cystine linkages. It has been noted that while steam can cause such opening, the subsequent closing of these bonds apparently in less orderly fashion, had caused embrittlement. Thus, cystine modification by commercial "permanent" treatments, thioglycolic acid, thiourea and the like were investigated and the products were examined for brittleness. Actually, these cystine altering operations had displayed little or no advantages for fixing the curl or without causing serious embrittlement. Many other chemical treatments had been surveyed, either for their stabilizing effectiveness or for their ability to impart other desirable properties. Thus, such other processes, as chlorination, bromination, iodination, oxidation and reduction have been applied to feathers. Reactions involving amine, acid and active hydrogen groups have also been investigated. Only minor advantages were noted for halogenation and nitrous acid treatments while the reaction with formaldehyde either did not take place or served no useful purpose. A cross-linking reaction was considered desirable to accomplish the needed stability but inasmuch as such was not accomplished with formaldehyde, the more reactive dialdehydes were investigated. Fortunately, glyoxal, the first of a series of dialdehydes studied, displayed not only high reactivity toward feathers but also an ability to further cross-link after drying to bring about outstanding stability and a degree of water repellency not obtainable by any surface treatment.

[See references 24, 32, 33, 34, 35, 36, 37, 38, 39, 64, 65, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 81]

a. *The Glyoxal Treatment of Feathers*

(1) *Stabilization.* Various concentrations of glyoxal have been applied to feathers but no difference in reactivity or stabilizing effectiveness has been noted at constant temperature as the active glyoxal solution content was increased from 1 to 10 percent. With the normal 1 percent aqueous glyoxal solution, the treating is conducted experimentally to a feather at solution weight ratio of 1-2 pounds feathers to 40 pounds solution. The hydrogen ion concentration seems to be critical. At the lower pH (2 to 3), the glyoxal penetrates the feathers, whereas at the higher values (6 to 8), more extensive reaction occurs

but the reaction is largely confined to the surface of the feathers. Although the commercial glyoxal is normally acidic, aluminum sulfate or alum (iron-free) at 0.1 percent concentration is included in the treating bath to insure the lower pH level. The operating temperature for the glyoxal reaction has been varied from 90° F. to 180° F. For curl stabilization, however, the processing temperature must not exceed 130° F. when carried out under the conditions of mechanical agitation encountered in an Easy Washing Machine for the 30-minute treating period. Any changes in these conditions would require adjustments in the temperature and period of operation. The influence of the glyoxal treatment at elevated temperatures on the feather properties is considered in this same section, Part (b) (j).

The glyoxal treatment of whole feathers, either of the preferred immature types or of the tri-sodium phosphate pre-treated immature and mature types, has been extremely effective in fixing the curl formed during relaxation drying. The glyoxal reaction is not presumed to produce the curl. Rather, this reaction fixes the curl probably through internal cross-linking with the amine and/or imide of the feather keratin, brought about during drying as a result of the pre-treatment. Almost invariably with satisfactory raw material, the glyoxal treatment has produced under laboratory conditions feather products of filling power above 5 cm. and as high as 6.8 cm. When, in a few instances, lower filling power materials were produced by the laboratory glyoxal treatment, the cause was traced to the type of raw material, poor pre-treatment or unsatisfactory drying and/or curing or fractionation conditions.

The drying and curing operations are especially important. Complete feather relaxation during drying is necessary to achieve optimum curl development and a cure or heat treatment, following complete drying, is needed to bring about the cross-linking so important for curl fixation. The curing of glyoxal treated feathers is accomplished by heating the dried feathers to at least 180° F. for 5 minutes. Fractionation is especially necessary to exclude large (wing and tail) feathers from the product.

The poor filling power for some glyoxal treated feathers made in the laboratory and most likely for preparations made in the plants is largely attributable to the drying and curing operations. In every sample in which unusually high bulk properties were provided by the laboratory technique, the product was removed in relatively small portions from the fluffer (Plate V) [58] immediately as dried and then either air or oven cured. If the mostly dried feathers were retained in the chamber while additional wet material was introduced, then the moisture from the latter samples apparently served to plasticize and alter the form of the first dried product. Other features of the operation such as the adherence of product to the walls as a result of electrostatic charge, and fractionation, have had some influence on the bulk properties, but all available data support the belief that the feathers must be dried quickly, must be removed from contact with

moist air quickly and then cured, if optimum bulk features are to be achieved. These observations are believed to be most important in explaining the variability in laboratory results and the normally poor bulk improvement achieved in plant trials. Ordinary drying facilities used in the laboratory or available in feather plants fail to fulfill the conditions indicated. Actually among the drying processes used on feathers, tumble drying[54] more nearly approaches the desired

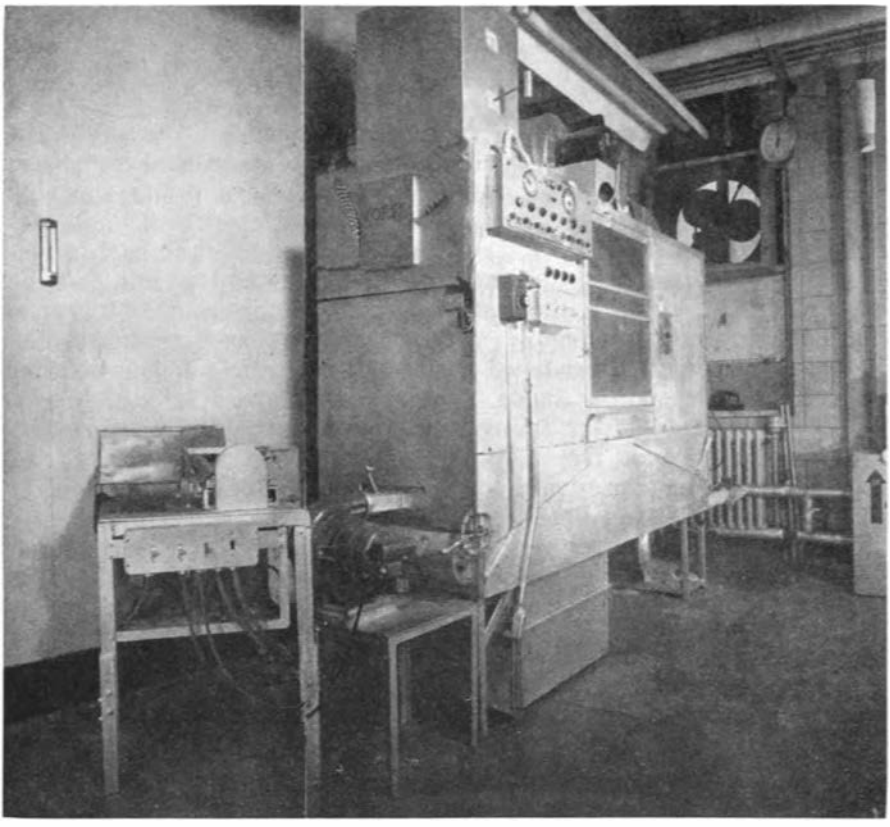

PLATE V

The laboratory picker, fluffer and drier

requirement. Under these conditions of operation, a large volume of air carries out moisture through the tumbling cage while the feathers are allowed to relax in contact with the incoming dry and heated air. The ideal drying operation would remove excess water from the feathers while they are allowed to relax completely. Immediately as the feathers lose this excessive amount of water and become sufficiently light and fluffy to be carried away from the wet feather, fractionation would take place to deposit the partly dried feathers into

a region, such as on a conveyor belt, for complete relaxed drying and curing, possibly by means of radiant heating.

The Easy Washing Machine, used so successfully for laboratory glyoxal treatments, provides a swirling action in an all aluminum tank by an aluminum agitator and wringing by an all aluminum spinner basket. When certain other treating tanks or facilities offering poorer agitation were used, the level of bulk improvement, as noted by the glyoxal treatment of feathers in the Easy Washing Machine, was not attained. In iron equipment, poor results have been consistently noted on feathers treated with glyoxal, and the inclusion of iron strips during exploratory treatments in porcelain equipment has proved disadvantageous. These observations regarding iron interference in pilot plant scale iron equipment are confirmed by experiences with the glyoxal process in commercial facilities containing unprotected iron parts. Apparently then, iron interferes with the glyoxal-feather keratin reaction. Commercial experience with the glyoxal reaction on animal glue used in cork binding seems to confirm the interfering influence of iron and this and certain other metals must also be eliminated in the regenerated keratin fiber (Rubberset) process. There still remains the possibility that the aluminum of the Easy Washing Machine has directly or indirectly favored the glyoxal-keratin reaction. The questions regarding catalyzing and interfering materials need to be answered. Chelating agents, such as certain Sequestrenes and Versenes, should be investigated as a means for eliminating interfering ions and/or for introducing catalytic ions in the glyoxal treatment. Chromium salts have been used in place of aluminum without ill effects, suggesting a need for a more general survey of the catalytic requirements in the glyoxal process.

A satisfactory degree of agitation appears to be quite necessary to achieve the desired curling action and curl fixation by the process. The influence of mechanical activity has been demonstrated in both laboratory and pilot plant operations on feathers and wool shrinkage has been shown to depend on this feature [23]. Invariably mild action has resulted in products of lower bulk properties than identical operations in which greater activity has been provided. The inclusion of feathers in bags during glyoxal processing in a commercial wash wheel (Plate VI) has restricted the development of optimum bulk properties and when the feathers are similarly confined during drying, no significant bulk improvement is noted. Mechanical agitating conditions can also be excessively severe as demonstrated by the fly and fiber development in samples treated for 30 minutes with the very vigorous action provided in the York Feather and Down equipment. While the type of mechanical action offered in any given equipment is critical, it will be obvious that the temperature and time of operation also determines the limitations for any given treating system. The mechanical activity provided by commercial feather processing installations varies considerably but this is not the all-important limitation

of such facilities. Recommendations of equipment for glyoxal processing of chicken feathers are given at the end of this section.

b. *Effectiveness of the Glyoxal Process*

(1) *Bulk Property Retention.* The glyoxal treatment has been applied to many samples and many types of chicken feathers to substantially upgrade bulk properties. Essentially all of the experimental

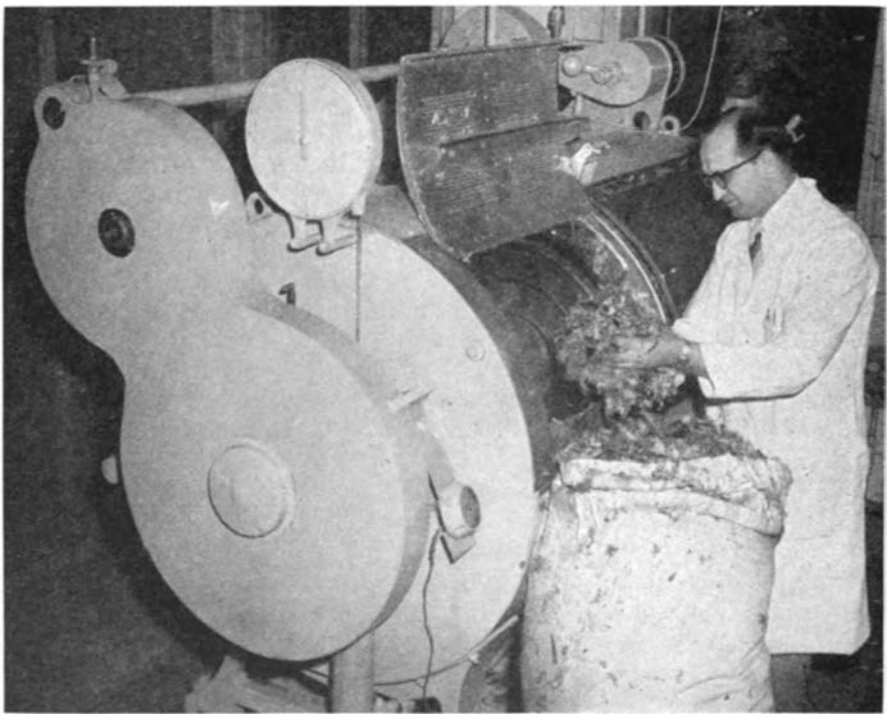

PLATE VI

Pilot plant feather processing equipment

products have measured at least 4.5 cm. When feathers have curled naturally (immature feathers) or when curled by means of alkaline phosphate treatments (immature and mature feathers), the process has yielded products of at least 5 cm. and frequently of 6 cm. or more filling power (Table X). Also, a relatively poor sample of goose feathers was significantly beneficiated by the treatment. The principal influence of the reaction in so far as bulk development is concerned, is that of fixing the curl formed by the conditions of pre-treatment. The chemical treatment may also serve to increase the stiffness of the quill, barbs and other feather parts. No embrittlement, however, has

been noted in glyoxal-treated feathers either immediately or several months after treatment.

That glyoxal stabilized curled feathers are permanently fixed has been demonstrated in laboratory studies of durability. These curl-stabilized feathers have returned to their high bulk form after having been held straight at room temperature and 100 percent humidity for several weeks or even after having been held straight between wetted blotting paper at 200° F. for several hours. According to laboratory studies, glyoxal curl-stabilized feathers possess outstanding memory, retaining their curl or returning to their curved quill form after these rather severe treatments. Unfortunately, only a very limited amount of data are available regarding the curl retention properties of these materials as enclosed in pillows or pads. Such experimental products have shown remarkable bulk properties after several months of moderate usage. Above all, these preparations have displayed a remarkable hand for chicken feathers, when an immature feather is used as the raw material. Ordinarily chicken feathers are known to be extremely harsh as a filling material, yet curl-stabilized, immature feathers possess a degree of softness that is, at least, equivalent to that provided by small waterfowl feathers.

(2) *Water Repellency.* Glyoxal-treated chicken feathers, without additional surface finish, approach waterfowl feathers in their water repellency. Such feathers may be dipped repeatedly in water without becoming wet. When so examined the water runs off or may collect as spherical water droplets, indicating an outstanding degree of water repellency.

(3) *Resistance to Microorganisms.* Glyoxal-treated chicken feathers display unusual resistance to bacterial attack. Ordinary wet chicken feathers, whether the raw material from an eviscerating plant or the washed product of a feather processing plant, develop foul odors from degradation by-products within a few hours. Glyoxal-treated wet feathers, however, have been stored in the wet condition for over three weeks without odor formation. Further evidence of the bactericidal qualities of these treated feathers has been provided from the odor test included in the specifications for waterfowl feather and down fillers. In this test, no odor must develop within 96 hours when a 5 gm. sample is stored in a quart jar and maintained at 100 percent humidity and 100° F. Waterfowl feathers and down and ordinary chicken feathers have consistently developed odors very soon (5 days), whereas glyoxal-treated chicken feathers have remained completely odor-free for more than four weeks storage at these conditions.

(4) *Durability.* Even the most ideally curled and curl-stabilized feathers would be of no practical usefulness if ordinary wear conditions and laundering caused significant degradation. Thus, the need for a thorough durability evaluation of bulk improved chicken feathers, and thus the laboratory attempts to conduct such estimations. As previously noted, the only satisfactory laboratory durability evaluation technique for bulk fillers seems to be the simulated wear tester or flex

tester developed earlier in this laboratory for examining interliner fabrics. A few samples of chicken feathers have been subjected to the conditions of the wear tester and compared with waterfowl feathers and waterfowl feather down mixtures similarly evaluated. These data presented in Table I, although inconclusive, indicate that glyoxal-treated feathers are not so embrittled as to be seriously degraded by the simulated wear test. Certain other treated feathers have been more severely affected but, because an accurate estimate of the relation between simulated wear and actual wear cannot be given, these results must also be judged with some reservation. Studies conducted by the Philadelphia Quartermaster Depot indicate that glyoxal-treated feathers do not break down by the Accelerator test to as great an extent as do waterfowl feathers.

The effect of an aqueous laundering operation on glyoxal-treated feathers is not serious according to the data provided in Table II, but more extensive studies on poorer samples, as conducted by the Philadelphia Quartermaster Depot, have not been so impressive.

[See references 36, 37, 38, 39, 40, 41]

c. *Commercial Glyoxal*

Glyoxal is offered commercially* as a 30 percent aqueous solution of glyoxal. The solution is a light yellow color, mild odored and is composed of a mixture of various hydrated forms of glyoxal and water with small amounts of the following chemically related substances that do not usually interfere with the action of glyoxal.

The type and concentrations of ingredients found in commercial glyoxal according to the analyses are as follows:

glyoxal	30.0-30.2 percent
formaldehyde	4.5- 5.5 percent
acid (as HCOOH)	1.6- 1.8 percent
ethylene glycol	8.0-12.0 percent

These included impurities are important primarily because they could interfere with the performance of the feathers if they were allowed to remain on the feather. Glycol, with its humectant qualities, would serve to pick up water. Accordingly, glyoxal treated feathers should be rinsed well before drying.

d. *Other Dialdehyde-Feather Reactions*

Two other dialdehydes are available although neither is yet produced in commercial quantities. Gluteraldehyde, a five-carbon dialde-

* Union Carbide & Carbon Chemical Company's Specification for glyoxal is:
not less than 30 per cent OHCCHO
specific gravity 20° C./20° C. = 1.20-1.28
color = light yellow
pH 20° C. = 1.5-2.0
average wt. per gallon = 10.48 pounds

hyde, and α hydroxyadipaldehyde, a six-carbon dialdehyde, are now being prepared in pilot plant quantities and potentially may be more available and more economically priced than glyoxal. Although gluteraldehyde has not been used for treating feathers, only because of an inadequate laboratory supply of the chemical, α hydroxyadipaldehyde has been applied to single samples of both whole feathers and feather fibers (Table XII). In each instance, significant improvement in bulk properties was noted. Pretreated whole feathers curled in the normal manner and the α hydroxyadipaldehyde served to fix the curl. These preparations are aqueous solutions of the dialdehydes and differ from glyoxal in that no appreciable quantities of impurities are included with the 25 percent solutions of the dialdehydes. Further studies of the launderability of glyoxal treated whole feathers and

Table XII

α-Hydroxyadipaldehyde Feather Treatment

Identification	Feather Type	Treatment[2]	Filling Power[1] cm.
Q-81	Chicken Feathers, Straight DM(I.R.)[3] immature partly fractionated	Haemo-Sol. Soak, 1% $Na_3PO_4 \cdot 12H_2O$ 1% α-hydroxyadipaldehyde + 0.1% $Al_2(SO_4)_3 \cdot 18H_2O$ TD[4]	5.9
Q-82	Chicken Feather Fibers, PQD	1% $Na_3PO_4 \cdot 12H_2O$+1.0% α-hydroxyadipaldehyde FD[5]	5.1

1. Standard Sinski Filling Power Test
2. Whole feather treatment—10 min. Haemo-Sol. Soak. 115° F.
   30 min. 1% $Na_3PO_4 \cdot 12H_2O$, 115° F.
   rinse
   30 min. 1% α-hydroxyadipaldehyde
   0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, 115° F.
   rinse, dry
   Feather fiber treatment— 30 min. 1% $Na_3PO_4 \cdot 12H_2O$, 115° F.
   rinse
   30 min. 1% α-hydroxyadipaldehyde
   0.1% $Al_2(SO_4)_3 \cdot 18H_2O$, 115° F.
3. I.R. = Indian River (most wing and tail feathers removed)
4. TD = Tumble dried—up to 180° F., 30 min.
5. FD = Fluffer dried—up to 200° F., 30 min.

α hydroxyadipaldehyde-treated whole feathers and feather fibers have been undertaken by the Philadelphia Quartermaster Depot. Preliminary studies on the treated fibers indicate that laundering does not reduce bulk properties but actually may lead to some slight improvement.

CHAIRMAN SCHUBERT:

The next paper is by Dr. H. B. Merrill and Mr. R. S. Adams. Dr. Merrill received his doctorate at the University of Wisconsin and has specialized in the chemistry of leather manufacture for more than thirty years. At present he is the Director of the B. D. Eisendrath Memorial Laboratory at Racine. Mr. Adams is a graduate of the University of Minnesota and has been engaged in research at the Eisendrath Memorial Laboratory for more than twenty years.

Owing to a coming meeting of the American Leather Chemists

Association, neither Dr. Merrill nor Mr. Adams could come. They have asked me to read their paper for them.

ANALYTICAL CONTROL OF CHEMICALLY MODIFIED CHICKEN FEATHERS

HENRY B. MERRILL AND ROBERT S. ADAMS

B. D. Eisendrath Memorial Laboratory, Racine, Wisconsin

The production of chemically modified chicken feathers will, eventually, require the adoption of physical and chemical control methods to ensure reasonable uniformity of the product. During the past two years, this laboratory has, on a number of occasions, been asked to make analyses of experimental lots of treated feathers. While the methods employed are not novel, some of them may not be familiar to analysts who are not leather chemists, and it was felt that the assembling of the procedures that we have used might be a convenience to other workers, and perhaps serve as a starting point for the development of a set of procedures to be incorporated in specifications.

The tests and determinations that we have made are exclusively chemical. We have done no work on physical or performance tests.

The determinations that we have made include pH value, fats (chloroform extract), ash, aluminum, iron, "acid sulfate," basicity of the aluminum complex, neutral sulfate, and chloride. We also determined vegetable tannin in some early samples that had been treated with sumac, and altho this determination appears to be of no interest at the moment, we are including a brief summary of the method used for possible future use. We have also tried, unsuccessfully, to determine glyoxal, and are reporting what we have done for the information of others who may be working on this problem.

Chicken feathers are so voluminous that handling them in the laboratory is something of a problem. We solved this problem by "pelleting" the feathers by feeding them into a one inch die and compressing them with a plunger in a Carver press. Pellets weighing 3 to 4 grams, thus produced, can be weighed, extracted, ashed, etc., without using out-sized apparatus, and without the frustrating experience of seeing half a weighed sample take wings when the balance door is opened.

The pH value of the feathers—more properly the pH of an aqueous extract thereof—presumably is important from the standpoint of the aging characteristics of the product. We determined the pH of solutions obtained by soaking 2 to 3 g. of feathers with 20 parts of a 0.01% solution of Naccanol, a well-known detergent, for 4 to 18 hours. pH values were determined with a glass electrode. This is the A.L.C.A. method for determining the pH value of chrome leather (5), except for the addition of the detergent, which was necessary to obtain proper wetting. Further, it is necessary to triturate the pellet of feathers in the Naccanol solution, using a stirring rod. The 0.01% of solution of Naccanol had a pH of about 6.5, and had practically no

buffering power. Presumably any other detergent possessing these characteristics would work as well.

pH values found for the various experimental lots that we have tested ranged from 3.15 to 6.8.

In some cases, it may be sufficient to make certain that the pH value is not below a specified minimum. For this purpose, tests with indicators, or test papers, applied to a pad of feathers (preferably white) that has been moistened with the Naccanol solution, may be adequate. The choice of indicator will obviously depend on the minimum pH that is acceptable. For example, if the minimum pH is to be 4.0, then the moistened pad should give a blue color with brom phenol blue (0.1%), while if the specified minimum pH is 5.0 the pad should give a green-blue to blue color with brom cresol green.

We determined fats by extraction with chloroform by the familiar Soxhlet procedure.

The ashing of the pelleted feathers presents no special problem. On occasion we have analyzed the ash for sodium, sulfates, and chlorides, to arrive at an estimate of neutral salts left in the processed feathers through inadequate washing.

Our procedure has been to determine aluminum plus iron gravimetrically as oxides, and to determine iron colorimetrically. Thus the aluminum is determined by difference. The ash of a 3 to 4 g. sample of feathers is taken up with about 5 ml. of 70-72% perchloric acid, diluted with 20 ml. water, warmed, and transferred to a 125 ml. Erlenmeyer flask. The contents of the flask are heated and evaporated till copious fumes are given off. This oxidizes the iron (and also chromium if any is present). The solution is diluted to about 75 ml., filtered into a beaker, and aluminum and iron are precipitated with ammonia in the usual way. The filtered and washed precipitate is dissolved in 1:4 HCl, and made up to 100 ml. (Solution A). Iron is determined in a suitable aliquot (usually 10 ml., less if the iron content is abnormally high) by the *o*-phenanthroline method (7). We prefer the reduction procedure with hydroxylamine. The procedure is as follows: Transfer 10 ml. of Solution A to a 100 ml. volumetric flask. Determine, by the use of a similar aliquot, containing a few drops of brom phenol blue indicator, how much sodium acetate solution (any convenient concentration) is required to bring the pH to 3.5-4.0. To the working aliquot add 1 ml. of 10% hydroxylamine hydrochloride. Then add the predetermined volume of sodium acetate solution. Add 1 ml. of 0.5% *o*-phenanthroline, mix, dilute to the mark, and determine transmittancy. If a spectrophotometer is used, the transmittancy is measured at 510 mμ; if a photocolorimeter is employed, the filter used should have maximum transmittance at 480-520 mμ. Calculate iron as Fe_2O_3 by comparison with a graph obtained by similar treatment of standard iron solutions. In another aliquot of Solution A, determine aluminum and iron together as oxides by the usual gravimetric procedure. Subtract the percentage of Fe_2O_3 from the total to obtain Al_2O_3.

Samples of untreated and treated feathers that we have examined mostly contained 0.03 to 0.05% Fe_2O_3, except for some plant-treated samples that were obviously contaminated with iron scale, and which ran much higher. The aluminum content of untreated feathers varied from 0.05 to 0.12% Al_2O_3; that of the treated feathers varied widely, as was to be expected in experimental lots, from 0.25 to 1.44%.

Leather chemists are wont to determine the degree of neutralization of the mineral tanning agent (Cr, Al, Fe, or Zr) in leather by determining the molecular ratio of "acid sulfate" (i.e., titratable sulfate) to the metallic ion. This, of course, assumes that the sulfate of the metal was employed in the tannage. A ratio corresponding to $Al_2(SO_4)_3$ is taken as 100% acidity (zero basicity); Al_2O_3 is zero acid (100% basic); the hypothetical compound $Al(OH)SO_4$ is 67% acid (33% basic). We have applied the American Leather Chemists Association method (6) for "acid sulfate" in chrome leathers to aluminum-treated chicken feathers. This method involves two gravimetric sulfate determinations. Total sulfate is determined in a solution obtained by digesting 2 grams of leather (or feathers) with 0.1*M* NaH_2PO_4 for 2 hours in a boiling water bath. The phosphate displaces all the sulfate complexly bound by the aluminum. The digest is filtered, and sulfate is determined gravimetrically in the filtrate. The total sulfate thus obtained includes any neutral sulfate (e.g., sodium sulfate) that may be present. Neutral sulfate is determined in a solution obtained by a similar digestion with water. As part of the acid sulfate hydrolyzes under these conditions, it is necessary to correct the sulfate found in the water digest by subtracting the acid sulfate found by alkalimetric titration of an aliquot of the water digest. If *A* is total sulfate found in the NaH_2PO_4 digest, *B* is sulfate found in the water digest, and *C* is the acid sulfate found by titration of the water digest (all expressed as % SO_4 in the sample), then

$$D = \%\text{ acid sulfate as } SO_4 = A - (B - C)$$

and % acidity of the aluminum compound is

$$\%\text{ acidity} = \left(\frac{D/48}{\%Al_2O_3/17}\right) \times 100$$

$$\%\text{ basicity} = 100 - \%\text{ acidity.}$$

If the sample contains appreciable amounts of iron, or chromium as was the case in some experimental batches, in addition to aluminum, then the mean acidity of the trivalent metal is gotten from the equation:

$$\%\text{ acidity} = \left(\frac{D/48}{(\%Al_2O_3/17) + (\%Fe_2O_3/26.6) + (\%Cr_2O_3/25.3)}\right) \times 100$$

Three samples of feathers that we tested gave basicities of 78, 88, and 95% for the total iron and aluminum present (plus a small amount of chromium in one case). The corresponding pH values of the aqueous extracts were 4.35, 5.1, and 5.85 respectively.

The method used by leather chemists for estimating fixed tannin in leather is to determine all other constituents (water, ash, acid sulfate, fats, water soluble organic matter, and collagen), and subtract the total from 100. This method is far from accurate, but since vegetable-tanned leathers usually contain very large amounts of tannin, an error of 1 or 2 percent is not intolerable. This method could not be applied to tannin-treated feathers, first because the conversion factor for converting the nitrogen content of feathers to keratin was unknown (at least to us), and second because the expected tannin contents were very small. We used a procedure for determining tannin in several lots of sumac-treated chicken feathers that is based on two facts: (1) nearly all the tannin can be stripped from vegetable-tanned leather with aqueous acetone (4); second, tannin can be determined quite accurately by a colorimetric method (1) developed by the present authors, providing that the *kind of tannin* is known. This method involves treating the tannin solution with a sodium nitrite and acetic acid, destroying the excess nitrite after 5 minutes by adding sulfamic acid, making alkaline with sodium hydroxide, and reading the optical density immediately at 400 mμ with a spectrophotometer. Percentage tannin is read off a curve obtained from solutions of the *same tannin,* whose tannin contents have been determined by the hide powder method. For details, the paper of Adams and Merrill (1) should be consulted. We applied this procedure to 5 lots of feathers, which, we were told, had been treated with 0, 0.5, 1, 2 and 3% sumac respectively. We do not know whether these percentages refer to the ratio of tannin to feathers, or to the concentration of the solution used for the treatment. Samples from these lots were degreased with chloroform, and then extracted 4 times with aqueous acetone (1:1). The fourth extracts gave only very faint tests for tannin with ferric sulfate. The combined acetone extracts were evaporated to dryness, and the residues were taken up in water. A considerable amount of each residue (0.7 to 1.5% of the original sample) was insoluble in water. This material, a white, finely divided sludge, obviously was not tannin, and was filtered off and discarded. The Adams-Merrill procedure for tannin was applied to the filtered solutions, with the following results:

Sample no.	1	2	3	4	5
Percent sumac used for treatment	None	0.5	1	2	3
Percent sumac tannin found in the feathers	0.002	0.94	2.22	2.74	3.1

These results are at least in qualitative agreement with the quantities of sumac applied, the percentages of tannin found rising with amount given, apparently approaching a limit at the highest amount applied. As the amounts found exceed the percentages given, it would seem that the percentages given do not refer to the ratio of pure sumac tannin to feathers, since this method for determining tannin in the acetone extract of the material must give values for tannin that are too low rather than too high.

We made preliminary experiments to see whether the method of Highberger and Retzsch (3) for determining bound formaldehyde in leather could be used for determining bound glyoxal in feathers. This method has been shown to be applicable for determining bound formaldehyde in rabbit hair (2). The method involves three steps: (1) decomposing the formaldehyde-protein compound with 2*N* sulfuric acid, (2) distilling the liberated formaldehyde into an excess of sodium bisulfite, and (3) determining the aldehyde by first titrating the excess bisulfite with iodine, then breaking up the bisulfite-aldehyde compound by adding sodium carbonate and titrating the liberated bisulfite with iodine. We believed that this third step, the double titration, should work with a bisulfite solution containing glyoxal, and it did. We had no pure glyoxal available, but a technical glyoxal, nominally 30%, assayed at 32% by this titration method. However, when we tried out the second step, that is the distillation, on glyoxal solutions treated with 2*N* sulfuric acid, we found that our recoveries, when the distillates were titrated, were very poor (not over 25%). Consequently, we did not study the first step, i.e., the decomposition of the glyoxal-keratin compound by boiling with acid.

Methods are outlined for determining pH value, ash, fat, aluminum, iron, basicity of the metal complex, and vegetable tannin in treated chicken feathers. An attempt to apply a method for determining formaldehyde in combination with protein to the determination of bound glyoxal was unsuccessful.

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CHAIRMAN SCHUBERT:

Our next paper is by Mr. L. E. D'Antonio. Mr. D'Antonio is chemist in the High Polymer Section of the Pioneering Research Division of the QM Research and Development Command here at Natick, working with Dr. Loconti who spoke yesterday. The title of his paper is "Alteration of Chicken Feather Geometry by Chemical Means."

ALTERATION OF CHICKEN FEATHER GEOMETRY BY CHEMICAL MEANS

LAWRENCE E. D'ANTONIO

Pioneering Research Division, Quartermaster Research and Development Command

Effective utilization of chicken feathers as a suitable substitute filler for waterfowl down and feathers, is ultimately dependent upon the mechanical and structural properties of the feather. The mechanical properties are those of elasticity, tensile strength, and stiffness among the barbs, barbules and rachis of the feather. In order that these properties will be most effectively brought into play in bulking action, it is essential that the feather parts be arranged with respect to one another so as to afford maximum contact and interaction.

This arrangement of the feather parts with respect to one another constitutes what we shall call the "geometrical structure" of the feather.

It is the purpose of this paper to point out some of the special structural arrangements desirable, the potential arrangements attainable and some of the basic chemical means for bringing them about.

For purpose of discussion here, no attempt shall be made to consider the effects of the chemical methods employed on the mechanical properties. Our primary concern is the desirable and necessary alterations in geometry and some of the "rationale" involved in bringing them about.

What are some of the basic structural differences between waterfowl down and chicken feathers which are reflected in their differences as bulk fillers and insulators? The answer to this question lies in the relationship between individual down filaments and feather barbs with respect to one another on a single unit, that is on a down cluster or chicken feather, and with respect to one another on neighboring units.

Some of the essential features of this relationship become apparent upon inspection. We have often heard the term "three-dimensional" mentioned in conjunction with the geometrical structural difference between down and chicken feathers. Down, we say, shows this "three-dimensionality" to a great extent, whereas chicken feathers possess it to a very small degree or not at all. What are some of the things which go into this "three-dimensional" arrangement, of what importance is it to bulking and insulating action, and what can we do to chicken feathers in order to bring about alteration to this form?

If one observes a single down cluster or several clusters together under low power magnification, that is about 45 × to 90 ×, several things are revealed (Figure 1):

1. The down filaments seldom contact one another's surfaces directly. As is noted in the diagram, this is due to: (a) the flexible nature of the filaments which twist and bend in several different directions (a. on figure), (b) the projection of filaments from a point source

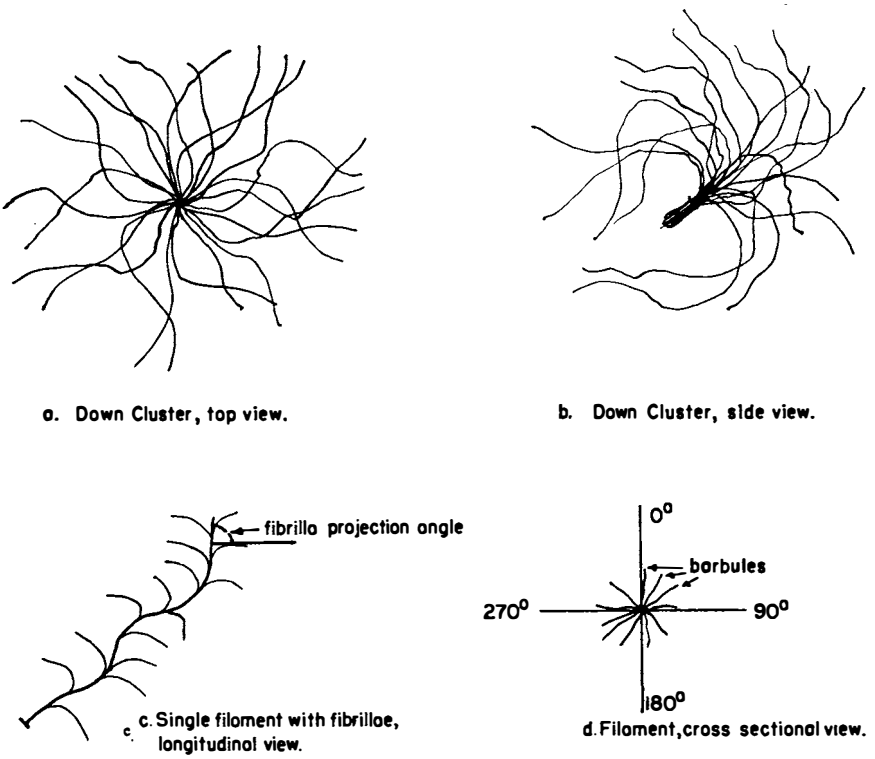


FIGURE 1

Down cluster and filaments.

into the many planes surrounding their point of origin (b. on figure), and (c) the projection of the small fibrillae almost perpendicularly from the filaments into the several planes about the longitudinal axis (c. and d. on figure).

The overall effect of the interaction of the down filaments within a given cluster or between clusters is dependent upon the way in which individual fibrillae contact filaments and other fibrillae; that is, by such means as point to point or point to surface contact (Figure 2). The presence of many individual clusters serves to multiply the effect observed between individual down filaments.

Chicken feathers, on the other hand, do not show the aforementioned type of interaction between filaments. As is depicted in Figure 3, this is due to the lack of "three-dimensionality" and is characterized by the fact that:

1. The rachis is essentially straight.
2. The vaned barbs are closely linked to one another, lying in the same plane and exposing only a large flat surface for interaction with other feathers (3a).
3. The fluff barbs project from the rachis into the same plane with little twisting or deformation into other planes (3b).
4. The barbules along the barbs project from the barb into the same plane and in the direction towards the tip of the barb (Figure 4).

a. Filament interaction, longitudinal view.

b. Filament interaction, cross sectional view from tips.

FIGURE 2

Down filament interaction—two views.

This geometrical arrangement of the parts results in an overall planar structure allowing very little opportunity for barb-barb or barb-barbule interaction between elements of the same feather or neighboring feathers. The overall interaction is that of gross surface contacts between units resulting in stratification and essentially little bulking action (Figure 5).

In order to create the "three-dimensional" form in chicken feathers along with increased filament interaction, as observed in the case of down, certain gross structural changes are necessary and possible. Among these alterations are to:

1. Impart (Figure 6) (a) curvature (6B), (b) twists (6C), (c) bends (6D), and (d) contractions (6E) to the rachis in order to minimize its presence or even use it to advantage in projecting the barbs into additional planes.
2. Increase the angle of projection of the barbs towards the perpendicular along the rachis (Figure 7B).

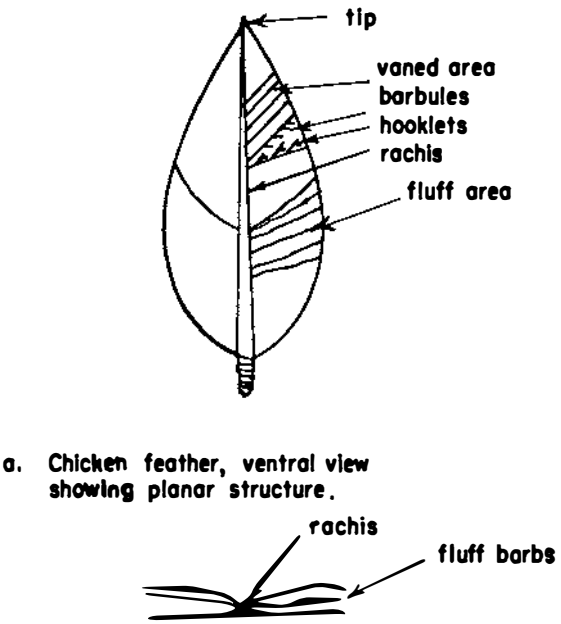


FIGURE 3

Chicken feather showing planar structure.

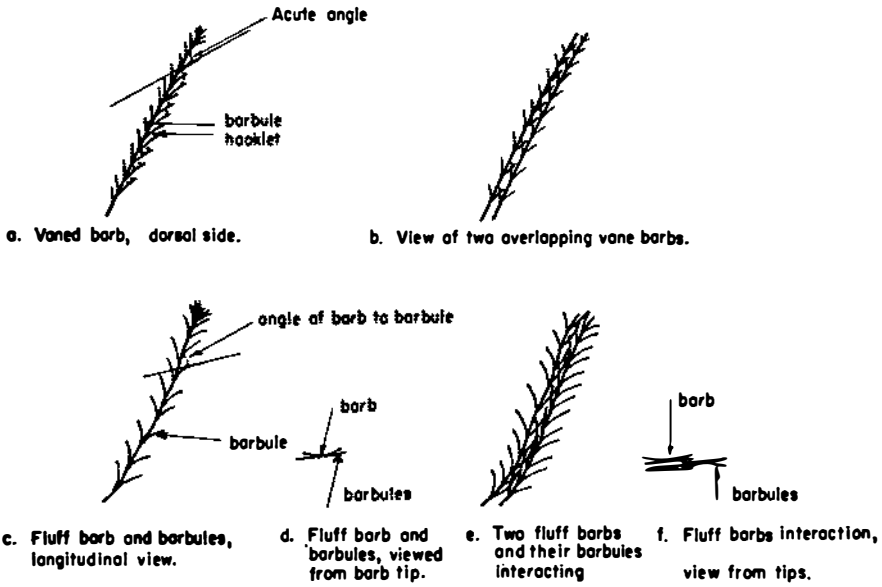


FIGURE 4

Chicken feather vane and fluff barbs and their interaction.

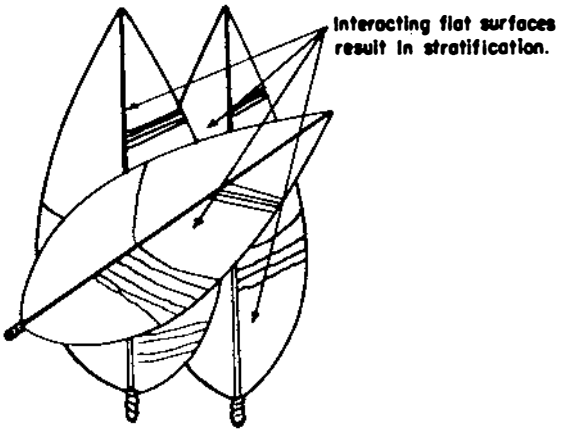


FIGURE 5

Planar structure of chicken feathers results in stratification.

3. Increase the number of planes longitudinal to the rachis in which the barbs project (Figure 7C).

4. Increase the angle of projection of the barbules towards the perpendicular along the barb (Figure 8, A and B).

5. Increase the number of planes longitudinal to the barbs in which the barbules project by (Figure 8, C and D) (a) imparting a twist to the barb, and (b) actual bending of the barbules.

6. Separate the vaned barbs by distortion or destruction of the hooklet linkages (Figure 8).

These alterations are represented by bends, twists, kinks, and contractions in the vaned and fluff barbs and barbules. Specific deformations may be brought about at several sites:

1. At the point of origin of the barbs along the rachis (Figure 9).

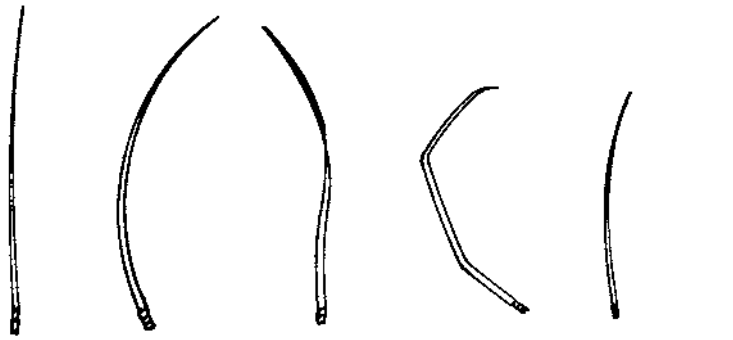


FIGURE 6

Alteration of feather rachis.

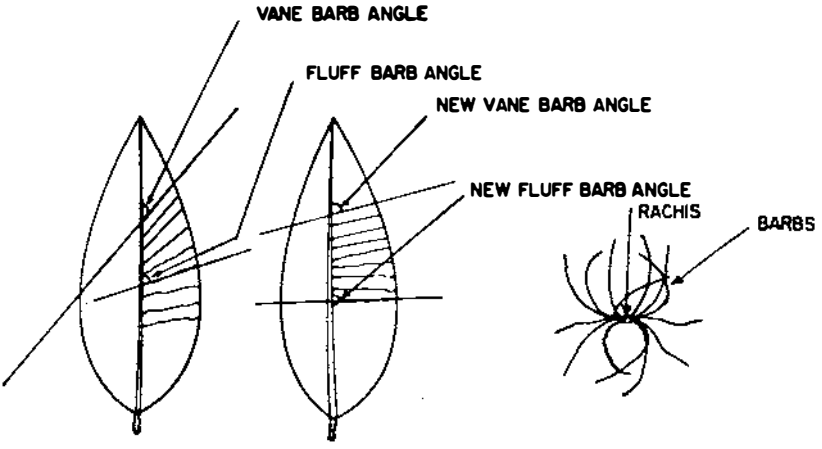


FIGURE 7

Alteration of barb-rachis angle and distortion of barbs into other planes.

2. Along the barbs (Figure 9).
3. At the point of origin of the barbule along the barb (Figure 10).
4. Along the barbule (Figure 10).
5. On the vane barb hooklets in order to facilitate separation of the vaned area (Figure 10).

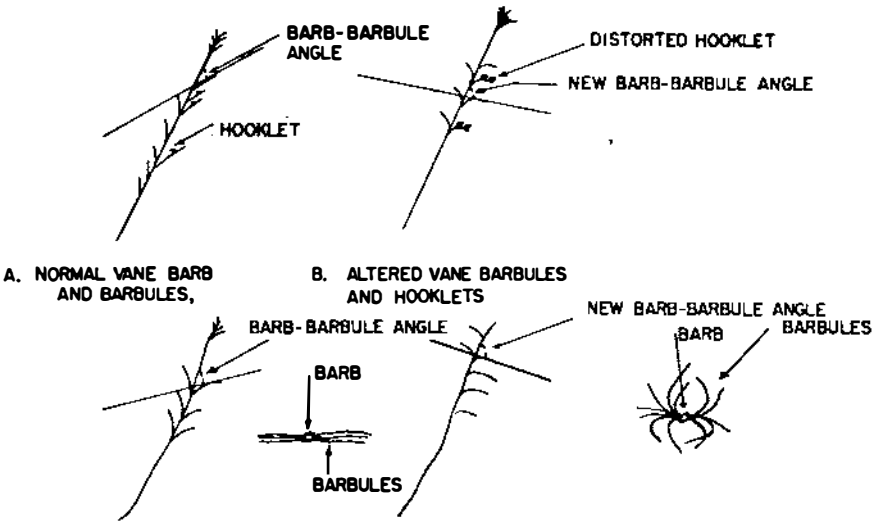
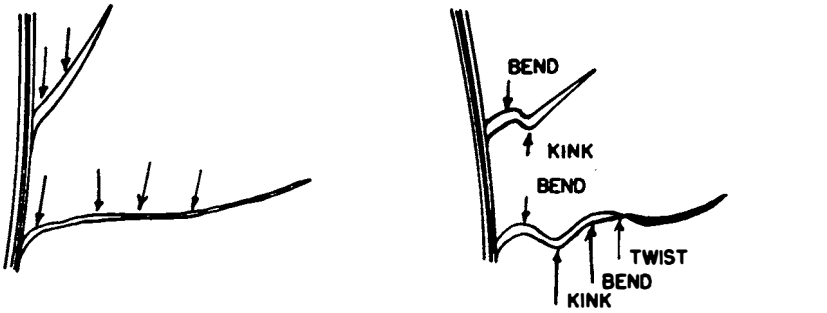


FIGURE 8

Alteration of fluff and vane barbs.

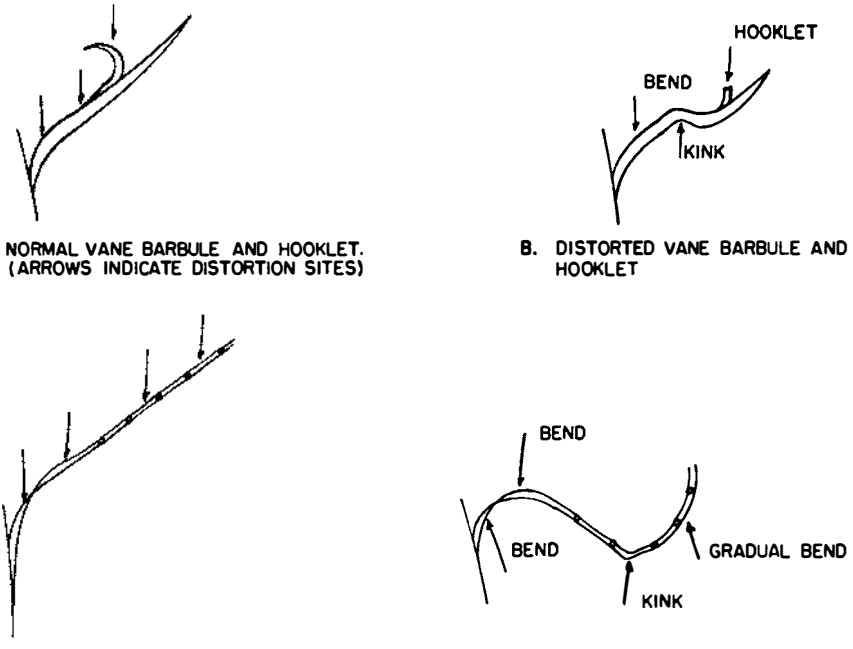


A. NORMAL VANE BARB AND FLUFF BARB (ARROWS INDICATE SITES FOR DISTORTION)

B. DISTORTED VANE AND FLUFF BARBS

FIGURE 9

Distortions on vane and fluff barbs.



A. NORMAL VANE BARBULE AND HOOKLET. (ARROWS INDICATE DISTORTION SITES)

B. DISTORTED VANE BARBULE AND HOOKLET

C. NORMAL FLUFF BARBULE (ARROWS INDICATE DISTORTION SITES)

D. DISTORTED FLUFF BARBULE

FIGURE 10

Distortion of fluff and vane barbules.

These deformations, as mentioned before, may take the form of gradual bends, sharp bends or kinks, twists, contractions or any combinations of these.

1. *Some Simple Methods for Inducing and Measuring Curvature along the Rachis.* Let us consider first some of the simpler methods for bringing about curvature changes in the rachis, along with methods for analyzing and comparing these changes.

It has been found that "on the average" the natural curvature of the

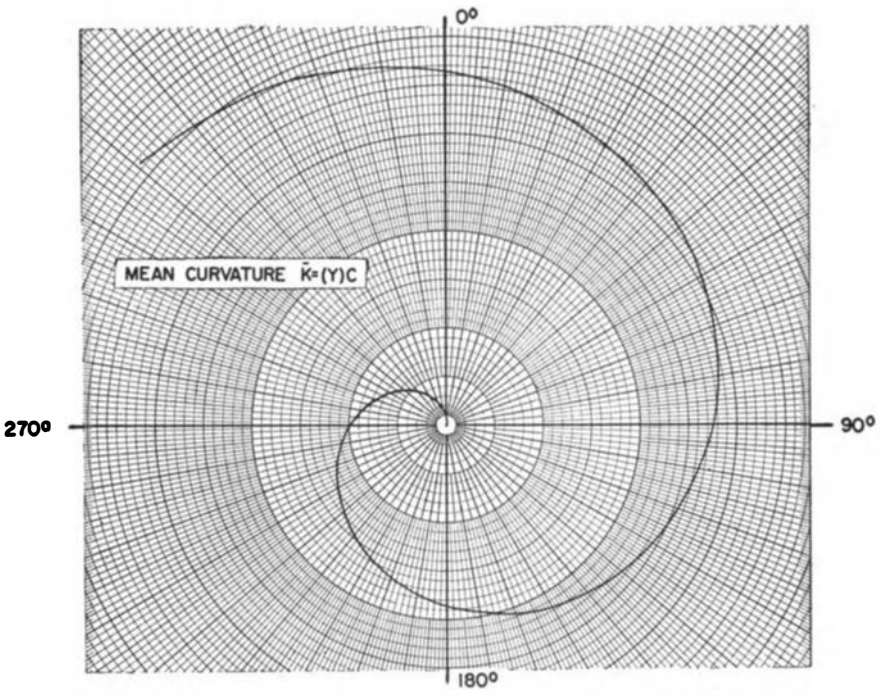


FIGURE 11

Spiral of archimedes R.

rachis most closely approximates one segment or another of an Archimedes' spiral. This is represented by the polar equation (Figure 11):

$$r = aO$$

Most moderate curvatures imparted to the rachis will approximate some segment along this curve. For purpose of comparative analysis of curvatures, the average or arithmetic mean of the individual curvatures existing from the root to the tip of the rachis is used. Since most of the rachises measured fall on a comparatively short segment along the spiral, the mean curvature represented by a rachis approximating a particular segment of the spiral is sufficient to give some

idea of the comparative magnitudes and a visual conception of the actual arc described by the rachis. This is depicted in Figure 12.

Table I shows the relative magnitude of mean curvatures observed on samples of untreated and mildly treated feathers.

From the table it will first be noted that regardless of the starting curvature under any particular treatment the final curvature falls in the same range for that treatment (Part A, Table I).

It is to be further noted that the final curvature imparted by water immersion seems to be independent of pH in the range from 2 to 9 (Part B, Table I). The pH range from 9 to 10 results in a somewhat

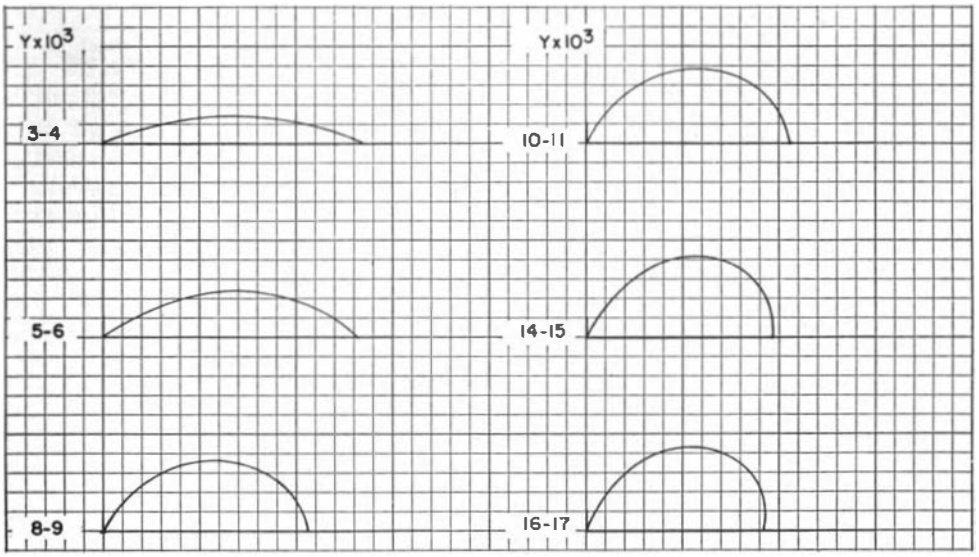


FIGURE 12

Arcs represented by mean curvature function Y.

greater and a bit irregular curvature. Since keratin is quite sensitive to pH conditions above seven we could expect more pronounced effects.

Part C of Table I shows the effect of immersion of feathers in boiling water for 15 minutes. The final curvature in the range of 12-14 is obtained regardless of whether the feathers were previously defatted by solvent extraction.

Part D, Table I shows the great difference in curvature between chicken feathers and duck feathers. The chicken feathers have a range of curvatures lying between 2.5 and 3.5. The duck feathers are much more highly curled, lying in the 10-15 range. These differences are partly reflected in filling power differences.

I would now like to discuss some of the more drastic means of bringing about chemical alterations. In the chemical treatment of feathers we have found that certain classes of reagents bring about certain

distortions to a greater or less extent. That is, one class of reagents brings about many kinks; another causes gradual bends; some merely increase the curvature of the rachis; others bring about much twisting.

The first type of treatment is that connected with the use of acid denaturants of proteins. Trichloroacetic acid, for example, has a very pronounced effect on feather structure. Immersion of feathers in boiling trichloroacetic acid solution causes the rachis to become completely

TABLE I

MEAN CURVATURES OF ARC DESCRIBED BY FEATHER RACHIS K Y C.

A. Original and induced curvature

Sample treatment	Original $Y \times 10^3$	Final $Y \times 10^3$
a. Immersed in distilled water pH 3, rm. temp., 90 hrs	6.00	9.9
b. Same as a. above	2.9	10.7
c. $CHCl_3$ extracted	4.1	6.9
d. $CHCl_3$ extracted	2.3	7.5
e. Boiled in water pH 5, 15 min	2.9	14.8
f. Boiled in water pH 5, 15 min	5.1	14.7

B. Final average mean curvature of chicken rachis on immersion for 90 hours at pH indicated

pH	Final range $Y \times 10^3$	pH	Final range $Y \times 10^3$
2	8-10	7	8-10
3	8-10	8	8-10
4	8-10	9	8-10
5	8-10	10	10-13
6	8-10		

C. Average mean curvature range imparted by boiling extracted and unextracted chicken feathers in water for 15 minutes

Treatment	Range $Y \times 10^3$
a. Unextracted, immersed boiling water[a] 15 min	12-14
b. $CHCl_3$ extracted, immersed boiling water[a] 15 min	12-14
c. Ether-alcohol extracted, immersed boiling water 15 min	12-14

D. Average mean curvature range of duck and chicken feathers

Feather	Range $Y \times 10^3$
Chicken (New Hampshire red fryer)	2.5 to 3.5
Duck (green pekin duck)	10-15

[a] pH-5.

distorted and the barbs are rather randomly distributed about the rachis. The overall effect is one of matting, with the feather full of kinks and bends. This reaction is dependent upon the acid concentration since more dilute solutions yield feathers having a much less drastic alteration in structure.

The trichloroacetic acid reaction is interesting from the standpoint of the geometric forms produced. It does not appear practical as a feather-treating agent since there is extensive damage as a result of peptide hydrolysis and the severance of salt linkages. An investigation into the nature of the damage is now underway and it is hoped

shall give some valuable information concerning the forces at work within the feather material. It may also give clues as to the best possible means of preventing or repairing the damage encountered.

The way in which a study of one particular reagent may "rationally" lead to a study of other reagents capable of bringing about desired alterations is exemplified by the simple step from the TCA and DNS treatments to the application of chloroform, a much milder yet effective reagent.

TCA is known to undergo decomposition in boiling water to carbon dioxide and chloroform (1), another well known protein denaturant (2).

$$CCl_3 \cdot COOH \longrightarrow CHCl_3 + CO_2$$

Extraction of chicken feathers with chloroform results in a change in the mean curvature function, Y, of the rachis from the 3-4 range to the 6-7 range of the Archimedes' spiral. A greater degree of fluffiness is also observed. This may be compared with extraction using diethyl ether or ethyl alcohol. Here the final mean curvature function is in the 4-5 range (Table II).

TABLE II

COMPARISON OF CURVATURES IMPARTED TO RACHIS OF CHICKEN FEATHERS

Treatment	Original range $Y \times 10^3$	Final range $Y \times 10^3$
None	2.5-3.5	....
Ethyl ether extracted	2.5-3.5	4 to 5
$CHCl_3$ extracted	2.5-3.5	6 to 7

Chicken feathers, refluxed in a mixture of chloroform and water for several hours at about 70° C., take on some of the three-dimensional qualities of TCA and DNS treated materials but without the ensuing damage such as weakness and embrittlement. Microscopic observation reveals the same bends, and curls along the fluff barbs and barbules and near their points of origin. Here, the vaned area is again undisturbed.

Indications that the chloroform plays an important role in the observed results are that similar treatment with water alone or in the presence of bromoform does not result in the same picture. It has also been determined that the chloroform treated materials on dialysis against distilled water contain about 0.3% chlorine as compared to 0.03% for untreated feathers.

Lithium bromide in concentrated solutions of from 50 to 70 grams per 100 grams of water is thought to act upon keratinous substances by liberating hydrogen bonds between such groups as carbonyl, amino, hydroxyl and so on. This is thought to occur in solutions where there is insufficient water since the strongly polar lithium ion which is ordinarily surrounded by a complete hydration shell in dilute solution is forced to coordinate with negative polarized groups containing hydro-

gen bonds such as hydroxyl or amino. The situation is thus one in which the lithium ion becomes highly competitive with normal hydrogen bonding(3).

Chicken feathers immersed for a period of 44 hours in a concentrated aqueous solution of lithium bromide (70 gm. LiBr to 100 gm. H_2O) at room temperature contract in all dimensions. The mild room temperature treatment distorts mainly fluff barbs and barbules with very little distortions in the vaned area. These distortions take the form of "kinks" and contractions. The deformations and contractions noted are reversible to some extent upon dialysis against water. If the lithium bromide is not removed from the feather shortly after removal from the solution, the contractions and deformations become irreversible. The vaned area also eventually becomes kinked under these conditions.

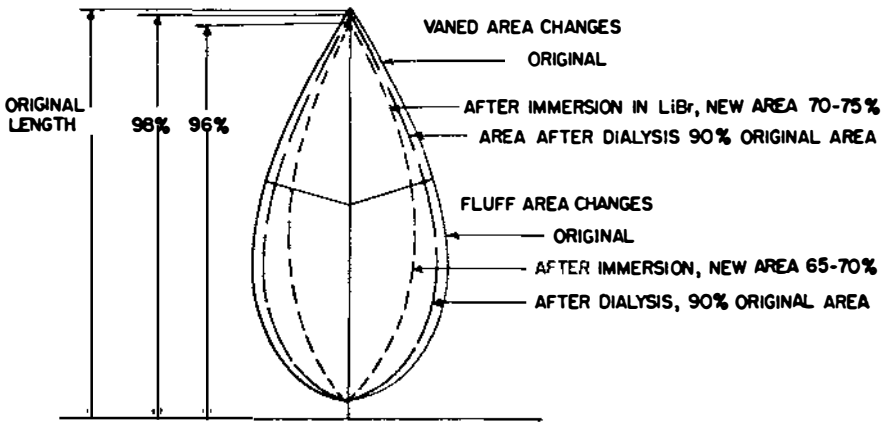


FIGURE 13

Dimensional changes of chicken feather induced by immersion in 70 gms. lithium bromide to 100 gms. water, 44 hours at room temperature.

As is noted in Figure 13 the rachis contracts by about 4% of its original length, while the fluff and vaned areas contract by about 30% to 35% respectively. The contractions among the vaned barbs are mainly due to actual length contraction along the barbs whereas that in the fluff area is the result of both length contraction and bending along the barb.

Dialysis of the lithium bromide restores the rachis to within 2% of its original length and the vaned and fluff areas to within 10% of their original areas. No change of curvature in the rachis is noticeable in the milder treatment described and is observed to occur only after dialysis. This curvature is the same as that determined for water alone, that is, between a mean value on the spiral of 8 to 10.

Treatment with lithium bromide at elevated temperatures (70° to

80° C.) results in irreversible twisting, curling and severe contractions in all parts of the feather, giving a matted appearance. This is accompanied by some weakening and embrittlement.

Aqueous solutions of potassium persulfate ($K_2S_2O_8$) have been found to bring about many favorable alterations without the severe damage accompanying other reagents causing equivalent changes such as moderate TCA or lithium bromide.

The extent of alteration seems primarily dependent on temperature and length of exposure. Concentrations down to 0.2% persulfate have been found to be effective. Concentrations up to 5% and 6% persulfate do not appear to change the type or extent of the alterations.

Treatment with persulfate at room temperature for about 40 hours produces bleaching of the normally brown feathers to a light yellowish brown. Form alterations are denoted by marked fluffiness and greatly increased curvature of the rachis to a mean value in the 14 to 16 range with many falling in the 18 portion of the spiral. In many instances the rachis takes on a twist along with the increased curvatures. Microscopic observations of the treated samples reveals spreading out of the barbules towards the perpendicular along the barbs, some twisting along the barbs, and the bending of the fluff barbs and barbules into other planes longitudinal to their stem of origin. Bending of the barbules is also frequently found. The vaned area as in other treatments does not appear altered.

Treatment at higher temperatures (70° and 90° C.) produces more accelerated and accentuated changes of the type described above. The rachis becomes curled, twisting of the rachis occurs frequently and to a greater degree, more individual barbs take on twists and bends and the barbules are bent and kinked more often along with more frequent bending at the point of projection into other planes longitudinal to the barbs.

Treatment of feather fibers have, of course, revealed the same geometrical distortions resulting in appearance of greater fluffiness and increased bulking capacity.

At this point we do not wish to comment too extensively on the actual mechanism of alteration or the nature of the chemistry involved. It does seem reasonable to assume that the oxidative potential of the persulfate is most surely involved(4). Persulfate is also a known free radical initiator (5) and it is conceivable that free radical formation does occur in the presence of the disulfide and sulfhydryl groups present throughout the feather proteins. The persulfate seems to bring about changes essentially unlike those brought about by other oxidizing reagents such as hydrogen peroxide and potassium permanganate. The latter reagents are quite destructive and do not result in the same overall appearance described for persulfate. This strongly suggests a selective oxidative reaction or other effects such as the free radical formation noted.

Our purpose here has been mainly to point out the chemical altera-

tions possible and desirable with the hope that they may point the way to:

1. Understanding the mechanism and chemistry of alteration, and
2. Presenting a "rational" approach to alteration with the ultimate hope of improving bulking and insulative properties.

It has not been the purpose here to discuss the other very important and desirable properties such as elasticity, compressibility, and strength. Before a suitable "product" may be claimed it is indeed necessary to have imparted all of these qualities. The "rationale" of alteration seems a reasonable starting point in the attainment of this final result.

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CHAIRMAN SCHUBERT:

The next paper is on "The Availability of Chicken Feathers as a Raw Material for Commercial Utilization" by Dr. C. H. Koontz. Dr. Koontz is the Assistant Director of Research for Swift and Company. He has spent most if not all of his life on problems pertaining to poultry. Last year Swift and Company would probably have elevated him to Vice President if he had developed a strain of bald chickens; now with the stated demand for feathers they probably will want him to develop chickens that will grow two feathers where one grew before.

AVAILABILITY OF CHICKEN FEATHERS AS A RAW MATERIAL FOR COMMERCIAL UTILIZATION

C. H. KOONTZ

Swift & Co.

We have heard a great many discussions about chicken feathers during the last two days. Somehow, one gets the idea that you may want chicken feathers at some future time. We have plenty of them here in the United States. We had only a modest amount of chicken feathers prior to about 1940. Then something happened in the poultry industry and the poultry population started to increase. The degree to which poultry production increased (1) may be observed in Table I. The number of chickens indicated in the tabulation includes

young birds and mature birds from farm flocks as well as broilers from specialized farms.

It will be noted that the poultry population has more than doubled since 1940. The increase in number of chickens has been linked with the growth of the broiler industry. Research has played an important role in the growth of this industry. Research has been responsible for the development of improved chicks, better nutrition, superior management, control of disease and better sanitation. In addition, research has been responsible for the development of improved methods of dressing, eviscerating, chilling, packaging, freezing, transporting, and merchandising poultry. These developments have made it possible to produce a pound of poultry at a cost that will permit the products to compete for a share of the consumer's dollar. Research then has been

TABLE I

SALES AND FARM CONSUMPTION OF CHICKENS—TOTAL [a]

Year	Number
1940	714,000,000
1941	802,000,000
1942	915,000,000
1943	1,159,000,000
1944	1,064,000,000
1945	1,158,000,000
1946	995,000,000
1947	963,000,000
1948	926,000,000
1949	1,110,000,000
1950	1,195,000,000
1951	1,376,000,000
1952	1,432,000,000
1953	1,501,000,000

[a] The Poultry and Egg Situation—USDA, Agr. Mkt. Service, Oct., 1954, PES-173, p. 5.

responsible for producing a product that is in demand by consumers.

Poultry and eggs today constitute one of the major agricultural commodities. The gross farm income for 1953 from poultry and eggs (2) was exceeded only by income from cattle and calves and dairy products. Approximately 15.7% of the farm cash receipts in 1953 were from cattle and calves, 13.7% from dairy products, and 12.1% from eggs and poultry. Livestock and products accounted for 55% of the total farm cash receipts. A breakdown of the income from poultry and eggs (3) reveals that in 1953 eggs constituted 58% of the farm value of poultry products. Broilers from specialized enterprises accounted for 20% of the farm value of poultry products.

Yes, the poultry industry is a large industry and we have a lot of feathers. The type of feather that we are talking about that may be useful in replacing waterfowl feathers may be seen in Figure 1. The percent of these usable feathers on broilers is approximately 4% of their live weight. This means that we have feathers by the bushel if you want them or by the trainload if you want them.

A rather accurate idea of the areas having the heaviest broiler population may be noted from observing Table II showing annual production of broilers for 1953(4). It will be noted that North Carolina, California, Delaware, Maryland, Virginia, Georgia, Arkansas and Texas have particularly heavy concentration of broilers.

It may be of interest at this time to comment on the current use of feathers. As pointed out above, approximately 4% of the live weight

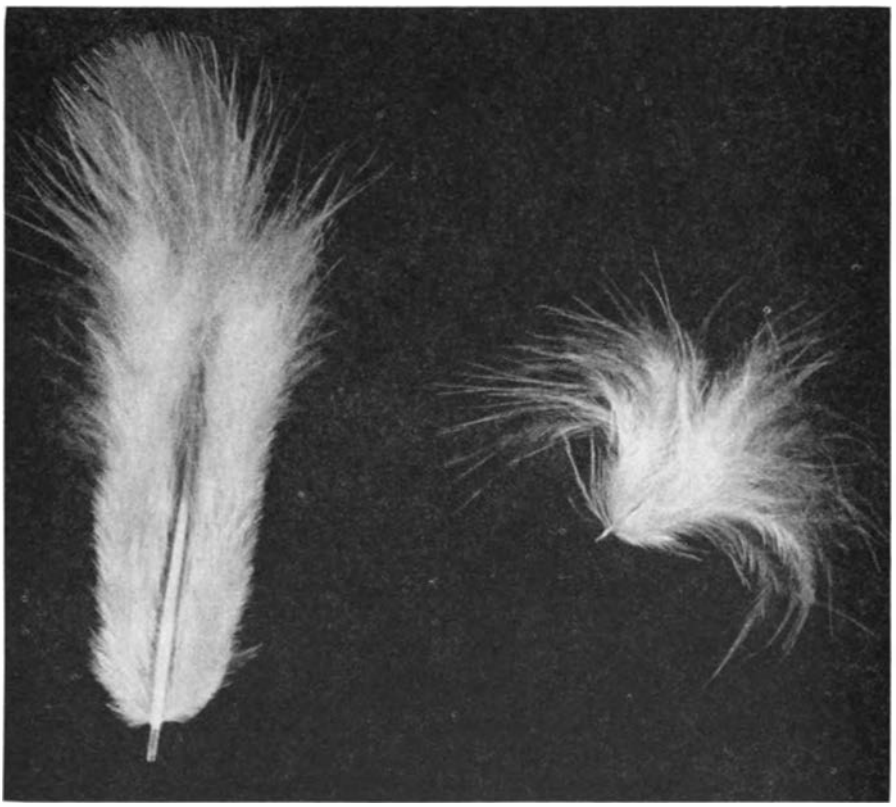

FIGURE 1

Chicken feathers—"body type."

of a broiler consists of usable feathers. The total U. S. volume of suitable feathers from broilers is approximately 120,000,000 pounds on a dry basis. This is figured on the normal feather weight as they come from birds not being subjected to water.

Chicken feathers currently have many uses such as in pillows, in millinery goods, and toys.

Some poultry feathers are processed so that they may be used in fertilizers. This product is sold particularly in the Southeast where the demand is for fertilizers which release nitrogen slowly.

There has been some interest in recent years in the use of feather meal in feeds. A patent(5) (No. 2,702,245) was issued on February 15, 1955, in which it was pointed out "the object of this invention is to provide a feed ingredient utilizing as the raw or starting material feathers from domestic fowl, such as turkeys, ducks, geese, and particularly chickens." The feathers are cooked for about 1½ hours at about 250° F. and 30 pounds steam pressure. Thereafter, the pressure control valve is opened and heating is continued for about 6½ hours until the moisture content has been reduced to 10-12%. It is reported that the resulting product shows about 13.96% nitrogen or 80-90% protein.

TABLE II

BROILERS: ANNUAL PRODUCTION, SELECTED STATES AND U. S. TOTAL[a]

State	1953 (mil.)
Maine	27.9
Connecticut	22.8
Indiana	33.7
Delaware	68.5
Maryland	62.1
Virginia	58.7
West Virginia	22.5
North Carolina	50.7
Georgia	121.6
Florida	10.5
Alabama	28.4
Mississippi	35.1
Arkansas	74.1
Texas	65.3
Oregon	4.9
California	48.6
Total 16 States	735.3
Total U. S.	985.8

[a] The Poultry and Egg Situation—USDA, Agr. Mkt. Service, Oct. 4, 1954—P'ES-173, p. 25.

Preliminary results obtained by Dr. Wilder of the American Meat Institute Foundation (personal communication, paper to appear in May issue of Poultry Science) indicate feather meal may be used in broiler feeds in limited amounts as a source of protein when supplemented with other proteins that offset certain inherent deficiencies. The experiments reported by G. F. Combs and G. L. Romoser(6), include rations containing some feather meal. Results appear to indicate the rations performed satisfactorily. The results of further investigations are needed in this area.

Actually, the volume of feathers until recently used for all the above purposes was relatively small.

Duck feathers, of course, are in demand. It is estimated that about 8,000,000 head of ducklings are produced currently and this should give a feather production of between 1 and 1½ million pounds annually with a value of between one and two million dollars.

It was earlier indicated that certain of the areas may be identified as being broiler producing areas, notably the Delmarva area and Georgia. It should be of interest at this time to note the volume of broiler feathers that are available in the principal areas based on 1953 annual production figures.

In the Delaware, Maryland, Virginia area on the basis of 1953 figures, there were approximately 23,000,000 pounds of broiler feathers available that could conceivably be transformed into feathers having water fowl characteristics. Georgia had 15,000,000 pounds, North Carolina 6,000,000 pounds, Arkansas 9,000,000 pounds, California 6,000,000 pounds, and Texas 8,000,000 pounds. This information is of special interest if we ever arrive at a place where a plant will be constructed for the purpose of transforming the physical characteristics of chicken feathers to resemble water fowl feathers.

From the standpoint of the poultry industry, it would certainly be desirable to find new outlets for feathers. It is hoped that it will be possible to develop a procedure whereby feathers may serve a useful purpose for the Armed Services and civilian populations.

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CHAIRMAN SCHUBERT:

The discussion of the various papers will be conducted by Dr. George F. Stewart. Dr. Stewart is Director of the Department of Poultry Husbandry at the College of Agriculture of the University of California. He is a member of this Committee as well as the Committee on Radiation Sterilization of Food.

Discussion

DR. STEWART:

It seems to me we've had a fine discussion, and it would be appropriate if we can manage to take as many questions as possible, not only those covering the talks today but also from yesterday. It seems to me we've just about covered everything there is. I was a little surprised to see—you usually wonder which comes first—I guess the chicken definitely came last here with Dr. Koontz's talk.

I might mention there are many interests represented here—not only research people, but industry people; not only those processing feathers, but those engaged in processing the chicken that results in these feathers. I would like to see some commentary, as well as some questions. I'm sure some additional information would be helpful particularly from people who were not in the program.

I suggest we go back to yesterday's program and particularly the afternoon session, and pick up any additional questions that might be appropriate here. Do any of you have questions on yesterday's session, particularly the afternoon?

I think we can start on today's discussion with questions. The first question is: In view of the general hypothesis that swelling takes place with increase in filling power, have any swelling measurements been made?

MR. D'ANTONIO:

The question, as I understand it, is: Have any swelling measurements been made in regard to specific chemical treatments? Unfortunately, we haven't carried our research to that point. We are quite interested in that problem, and I feel we will go into it rather thoroughly at a later date.

DR. LOLLAR:

I would like to point out that if by swelling you mean the increase in greater weight of the feather while wet—what I would mean by protein swelling—we're using that as a tool. We do find in our preliminary results there is some degree of correlation under increase of weight and the ultimate increase in volume of the dry feathers, if you use a constant and effective tumble drying.

DR. STEWART:

Any other comments? To Dr. Florio—four questions. First, how long does it take to neutralize?

DR. FLORIO:

It takes but a few minutes. There is not very much acid to neutralize. The twenty minutes reported is to make sure all the feathers assume a neutral pH. With good agitation, it could take five, ten or fifteen minutes. As I said before, we add the soda ash until the milky color just appears, because it becomes an easy thing to do commercially.

DR. SCHUBERT:

If you have an excess of aluminum sulfate, it might dust off after the feathers have been dried?

DR. FLORIO:

If you do add too much soda ash, you do have a possibility of dusting. Generally, the pH we arrive at is about 5.2. We use a concentrated solution of soda ash and water.

DR. STEWART:

Why did Dynel appear to be so good in compression measurements?

DR. FLORIO:

Partly because of high static and the ability to hold static a lot

longer than the feathers. Then too, Dynel has a low density and a high crimp ratio which also makes for better filling.

QUESTION:

Would you say Dynel has a better fill because you can't measure filling comparatively?

DR. FLORIO:

It has better initial filling power which may eventually disappear due to "pilling" or "balling" up of the fibers. It is possible in using the filling power test to measure comparatively.

QUESTION:

Did you try any synthetic fibers other than Dynel, or just Dynel?

DR. FLORIO:

We've used Dacron and nylon. Dacron is probably the best of all. The important factors are density, fiber length, and fiber crimp.

QUESTION:

What about denier? Does denier make a difference in filling power?

DR. FLORIO:

From our experience in making yarn, it does. All things being equal that is, both density and crimp, the lower the denier the higher would be the degree of bulking, although the resiliency may not be improved.

QUESTION:

I think it might be interesting if some of the people in industry would comment on the use of synthetics instead of feathers and down.

DR. STEWART:

Are there any comments on synthetics for general use? Anybody want to comment?

ANSWER: I'll say, they're being used but only as a poor substitute.

MR. LERMAN:

In one of your experiments you used duck feathers, and basically they had more filling capacity. I wonder if you applied your "Keracurl" test to used duck feathers.

DR. FLORIO:

No, we didn't because when feathers get to a point in use where their filling power or their ability to compress and release is lost, then we believe there's been a chemical degradation involved. Using "Keracurl" might improve it; but we don't know how long it would last.

MR. LERMAN:

I think it might be a good idea if you did.

DR. STEWART:

Why use minimum thickness for measurement?

DR. FLORIO:

Minimum thickness is used because it is the only way to obtain a measurement free of any side effects. A small template is placed on the feather charge and it is used to level off the top feathers as well as put them down into a sort of loose batting. The thickness of the batting is taken as our measurement of bulking power, that is, after the piston hood has been removed.

QUESTION:

Wouldn't that tend to penalize certain materials?

DR. FLORIO:

You want to get differences between the materials; you want to show positive differences in which your compression and release is an important factor. In order to get a figure with meaningful results, you have to have some load on it. Otherwise, the surface you're measuring is completely unoriented.

QUESTION:

I presume, in measuring minimum thickness, the load is constant.

DR. FLORIO:

That's right. To what extent the feathers will support a load is what we're really measuring.

DR. STEWART:

What is the cost of the installation of the equipment you recommend?

DR. FLORIO:

If you have the equipment such as is used in industry and the space allocated, then, to convert to this process and put in a completely new drier, conversion would run between thirty and thirty-five thousand dollars.

DR. STEWART:

Any other questions?

MR. LERMAN:

In reference to the equipment on the rotary drier, you have the direct heat coming through a screen?

DR. FLORIO:

It's a screen cylinder.

MR. LERMAN:

For practical uses, I don't think in a commercial field that would be very much applied to feathers because you would get the feathers to clog into the screen, and, if you have that, you wouldn't get an even flow of heat. And, also, a lot of seepage of the fine feathers and pith to clog up the heating regulation; I don't know.

DR. FLORIO:

We have a small scale drier like the one pictured. You can use a two hundred mesh screen where the feathers wouldn't impinge. The heating unit is placed underneath so that the heat passes through the box by means of baffles, and the stream of hot air has a tendency to pick up the feathers right off the bottom part of the screen; this also avoids impinging the feathers into the screen itself. There are other ways of doing this job, but we merely suggested this method of doing it. The important thing is to have them dry them without any constraining forces. You can do it by drying in a big bowl by blowing air into it, or by using a regular calciner type drier.

QUESTION:

What mesh screen do you use?

DR. FLORIO:

Two hundred mesh.

QUESTION:

What capacity?

DR. FLORIO:

For this drier, I don't remember the length of it, but this particular drier, which would run about ten thousand dollars without installation would operate at about two hundred fifty pounds of feathers an hour continuously, putting in one end and taking out the other.

QUESTION:

Is the "Keracurl" process applied to raw chicken feathers or are they given preliminary washing or dusting?

DR. FLORIO:

The process is applied to all kinds of feathers, whether detergent-washed or off the chicken's back. It operates just the same; there is no preliminary washing necessary.

DR. STEWART:

Of the various feather components which affect filling, which would you say is the most important in improving filling in the chemical process?

DR. FLORIO:

From our experience, we do two things to the feather. One is fluff the feathers; we add something to the feather that prevents the fluff parts from getting close to each other and repel each other. And, we curl the feather; we curl the quill which laps over on itself. We think that produces the greatest difference, because fluffing it and keeping it straight wouldn't give you half the filling power. We think the curl represents a three-dimensional change of an inch or two, where fluffing may give only an inch in thickness.

MR. D'ANTONIO:

I believe that you have to consider first of all why we're interested in filling power. If we're interested in relating filling power to insulating properties, I'm not too sure the presence of a curled rachis is going to help insulating quality. It will give instant filling power, but we're interested in keeping the air space to a minimum. I'd say fluffing the barbules gives greater inner-action, consequently less air pocket formation. Insofar as the filling action goes, our treatments indicate treatment on fluff alone, fibers taken off the rachis—the whole feather with the curled rachis will give us the edge on filling power. I'm not convinced that's desirable as far as insulation goes.

DR. STEWART:

They've asked for comparison among the three processes in relation to the same problem.

MR. D'ANTONIO:

I have not closely investigated, but I described "Keracurl" process. I have run a reaction using gluteraldehyde in place of glyoxal, and I find there is an increase in the curvature. I'd say the curvature of the

first is less than that of the persulfate treated feather. I would say the fluffiness of the persulfate initially exceeds that of the first.

QUESTION:

In these three methods, what is the mechanism by which they each produce the increased filling power? Do they all operate mainly because of bending the rachis?

MR. D'ANTONIO:

Undoubtedly, each method produces this fluffing effect. Each method does curl the rachis to some extent. All the factors come into play; we haven't isolated each factor, but should.

QUESTION:

In the diazo process, do you believe there is a higher bulking or filling power? In other words, what made you use the diazo compound in the first place?

DR. LOLLAR:

We wanted to add a group to the feather which would have the ability to enter into the sphere of metallic tanning salt. It looked like the diazo reaction offered a way to do it. It was to try to get an increased tanning function. With reference to what the subject treatment is doing to the form of the feather, the increase in what has been called the fluff of the feather is very large. In this case, there is also a rather large amount of spiraling of the rachis, perhaps more important than the curvature. As I said yesterday, the increase in fluff as it distorts the barbs has been contributing quite a bit to it; but, I can't say which is more important. I can't say the contribution of the barbs is more important.

DR. STEWART:

What does a curing operation do to the filling power or bulking properties?

DR. FREDERICK:

We've assumed that it effectively caused the stabilization of this new form. And, in glyoxal reactions, it means that there is a two-stage operation—first, the tie-up with the amine; and second, the elimination of water. It appeared to us it would be necessary to cure it. The only basis we've found for cure or non-cure is there is a slight increase by curing. Room temperature caused the reaction to apparently proceed satisfactorily, twenty-four hours or what have you, but there is a tendency of a difference of four- or five-tenths of a centimeter.

DR. STEWART:

Has any consideration been given to the improvement of sewability in the end item when chicken feathers are used as a filler? Penetrating quills have been a major problem to the manufacturer of sleeping bags.

ANSWER:

The only thing I'd like to mention about fiber penetration is again this physical character of the barbs and knots, and they do apparently tend to resist motion. We don't have those knots on chicken feathers. They are more pointed and slick and move more rapidly. The same

has been true of wool and some other materials in our clothing. On the question of sewing, I have no comment.

DR. KENNEDY:

The answer I think is, if we develop a satisfactory chicken feather, we would go back to the low type of filling and not use that method of making sleeping bags.

QUESTION:

To Mr. Weiner, on the filling power chart—it's a very interesting chart where you show the different filling powers of the different European geese, etc. I was wondering if you can tell us whether you took the samples or whether they were sent in, because I've been in contact with the different types of downs and don't seem to be able to get the type of filling power you indicate on these charts.

MR. WEINER:

What type of filling powers have you been getting?

ANSWER:

On the European, I've been getting up to nine. I notice in your charts you had from ten to twelve. It may be the technique in the filling power test is not perfected, or there are errors in it.

MR. WEINER:

We have a class of down in our specifications for waterfowl feathers and down, that requires that the filling power must be a minimum of ten.

QUESTIONER:

That was based probably only on your samples which indicated a certain filling power.

COMMENT:

I'm going to ask a very pointed question. Have they been done under conditions of temperature-humidity? I can't believe yours have been done in that way.

QUESTIONER:

Right.

COMMENT:

Unfortunately, and I'll agree with what is being implied, some of those samples might have been Sunday samples because, some of the results in the duck category, we have not ever been able to duplicate nor have people in other laboratories; and I know requests to different manufacturers were sent out, and I don't think some of those tables are accurate as they stand, but the range is correct. You can get filling powers of above ten with the good stuff.

DR. STEWART:

There is room for arguing on standards of testing, but time is running on, so I'll turn the meeting over to Dr. Schubert for summary.

CHAIRMAN SCHUBERT:

My summary shall be brief in order that we may close the meeting on schedule.

This conference has been a pioneer project in its field. The papers

which have been presented should be of interest and value not only to the scientist but to industry, such as the convertors of chicken feathers, manufacturers of clothing, bedding, insulation and even those interested in imitating expensive furs such as Persian Lamb from low price domestic lamb skins.

The papers presented by Drs. Stahl, Low and Krimm are of basic or fundamental interest. They give the worker who is interested in basic research much food for thought and stimulation for further experiments. Dr. Loconti's paper enables us to intelligently realize the possibilities of chicken feathers. Mr. Weiner has shown us what has been as well as what needs to be done in order to give the Army what is needed. From the paper by Dr. Lollar we obtained data as to the effect of preliminary treatments and in addition we see that there is a strong possibility that we may be able to produce a product which will be better than today's standard (waterfowl feathers and down). We see that it may be possible to obtain a new product from chicken feathers which can be used by itself and will give better insulation and warmth than waterfowl feathers and down.

Drs. Florio and Frederick have shown how on a laboratory scale chicken feathers can be treated so that they will more closely approximate the properties of waterfowl feathers and down.

Mr. D'Antonio has shown the relation of structure or construction of feathers to filling power and Dr. Koontz has shown that there is no danger of a shortage of chicken feathers, rather that their production is on an increase.

I thank you for your interest and attendance at this conference, also for your contributions in the discussions. The results of this conference will be seen in the future and I am hopeful that concrete results in the application of some of the ideas presented here will not be far off.

This conference is now ended and we will stand adjourned.

DR. KENNEDY:

I should like to say that we in the QMR&D Command are very deeply indebted to all of you, and to the National Research Council for sponsoring this conference. We are grateful to you for coming, and to the speakers for the very stimulating and suggestive ideas they've given us for future research in this field. We hope that out of this will come something very constructive and helpful to this part of the National Defense program. We will publish all of these papers in a consolidated volume, and all persons attending will receive copies automatically. Otherwise, copies will be available through normal channels.

Again, we have appreciated your coming and, on behalf of General Calloway and the staff, I want to say thank you and hope you will come again.