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TRENDS IN USAGE OF CADMIUM

REPORT OF
THE PANEL ON CADMIUM
of the
COMMITTEE ON TECHNICAL ASPECTS OF CRITICAL AND STRATEGIC MATERIALS

NATIONAL MATERIALS ADVISORY BOARD
Division of Engineering - National Research Council

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INTRODUCTION

Cadmium is a silver-white metal which is relatively rare and is found in small amounts in zinc ores. It was discovered in 1817 by Professor F. Strohmeyer as an impurity in zinc carbonate. Historically, the chief use of cadmium has been as an electrodeposited finish for corrosion protection. An important modern use is as a pigment in paints where cadmium sulfide in various forms or combinations with other metal sulfides serves as the basis for many yellow to red shades. More recent applications are as an anode material in the nickel-cadmium alkaline battery, as cadmium oxide in silver-cadmium oxide for moderately high-current electrical contacts, as a constituent in certain high- and low-melting solders and brazing alloys, and as one constituent in stabilizers for polyvinyl-chloride polymers. Applications which consume lesser amounts of cadmium include standard cell manufacture and a hardening agent for copper in automobile radiators. Certain electronic applications are of modest importance. These include cadmium sulfide for photosensitive electronic devices and for cadmium-containing phosphors in television picture tubes.

I. Cadmium Supply

Cadmium is a relatively rare element with the earth's crust estimated to contain an average of one-half gram per ton. Fortunately, for recovery purposes, much of the cadmium is associated with the extensively mined zinc sulfide mineral, sphalerite. Zinc concentrates from sulfide ore deposits contain up to 1.4 percent cadmium. Cadmium is recovered almost entirely as fume or flue dusts during roasting, sintering, and smelting of the zinc concentrates. A small amount is also recovered as flue dust at lead and copper smelters processing complex sulfide ores.

Thus, production of cadmium is associated with zinc refining plants and with zinc producing countries. Significant production is posted by 22 countries in the world. Annual production in recent years has ranged from 26 to 29 million pounds. Recovery of cadmium as a byproduct of zinc ranges widely by country from less than a pound per ton of zinc for Zambia to over 8 pounds in the United States and Japan. The average for the Free World during the period 1964-1967 was 6.5 pounds of cadmium per ton of primary zinc produced. The 10.4 pounds indicated as an average for the United States include imports of Mexican flue dust, whereas recovery from domestically-refined zinc is indicated to be 8.8 pounds.

The association of cadmium with zinc necessitates consideration of future supply in terms of zinc output and reserves in the Free World. The individual country fluctuations in zinc production and cadmium recovery, of course, are factors meriting a detailed discussion beyond the scope of this study.

Free World zinc mine production has increased from 3.1 million short tons in 1962 to 4.3 million in 1967. Capacity is projected to 4.5 million short tons in 1971. Announced increases are scheduled in most of the zinc producing countries, and zinc smelter capacity is expected to increase well in excess of mine production. On the basis of the Free World average cadmium output of 6.5 pounds per ton of zinc, the projected supply would increase to 29 million pounds in 1971 and represent a 7 percent annual growth after 1967. Availability of cadmium in the various consuming markets is dependent on smelting capacity and the availability of zinc concentrates from both domestic and import sources for each individual country. The United States is dependent on imports of zinc concentrates for approximately 40 percent of the cadmium, and on imports of cadmium-bearing flue dust for an additional 20 percent. Domestic ores thus contribute about 40 percent of the domestic cadmium production.

World zinc reserves have been estimated at 100 million tons, well-distributed throughout the zinc producing countries, and the more than 600 million pounds of cadmium indicate a continuing of the relatively inelastic supply dependent on the expansion in demand and productive capacity for zinc.

II. Statistics

Because of the nature of the cadmium market, a determination of the apparent U. S. consumption is best made through a combined analysis of total U.S. production, of the net of imports versus exports, and the changes in stockpiles. For this purpose, it has been decided to use the figures given in the Bureau of Mines Minerals Yearbook for 1967 with preliminary figures supplied for 1968. These are given in Table I. The above determination reflects changes in consumer stockpiles. In order to remove this yearly fluctuation, a running average of the last three years will be used. The average apparent consumption determined in this way for 1968 is 13,200,000 pounds of cadmium.

A discussion of prior surveys is also in order. A survey conducted by the U. S. Bureau of Mines in 1960 accounted for 74 percent of the apparent consumption of cadmium in the U. S. Of the quantity of metal accounted for, these figures indicated:

70% for plating (5.2 million pounds),
21% for pigments, compounds, etc. (1.6 million pounds), and
8% for alloys (0.6 million pounds).

Comparable figures for 1963 gave:

55-60% for plating,
30-35% for pigments, and
7-10% for alloys.

In 1963 it was believed that the percentage used in plating would decline within the next few years to about 50 percent, and the percentage used in pigments was also expected to decline. Increases were expected in compounds, nickel-cadmium batteries, and stabilizers for plastics. However, in 1967, best estimates still showed plating at 60 percent of a total apparent consumption of 11.6 million pounds (approximately 7.0 million pounds).

A recent analysis of the cadmium consumption pattern has been made by the U.S. Department of Commerce Business and Defense Services Administration for the year 1965. The estimate for the total consumption for that year was 10,431,000 pounds, which is identical to the Bureau of Mines consumption figure for 1965. The breakdown by categories is given below:

	In Millions of Pounds	% of Bureau of Mines Consumption
Plating	4.00	38.4
Pigments	2.56	24.5
Dies & Tools	1.26	12.0
Fuses	.14	1.3
Batteries	.72	6.9
Reagents	.85	8.1
Unknown based on Bureau of Mines Yearbook	.90	8.6

The consumption figures for the United Kingdom, as abstracted from "The World Metal Statistics" published by the World Bureau of Metal Statistics for the years 1967 and 1968, are included for information in Table II.

III. Metallurgical

Cadmium has several metallurgical uses. Each is discussed separately below.

A. Low Melting Alloys

Cadmium is a common constituent in low-melting alloys, and in this application is used in conjunction with other metals like bismuth, lead and tin. A 10 percent cadmium alloy is commonly used for potting blades in aircraft engines. The 1968 consumption is estimated at 80,000 to 100,000 pounds. It is possible that this use could increase to 150,000 pounds in several years.

B. Cadmium Usage in Electrical Contact Market

Silver-cadmium oxide is a widely used material in the electrical contact field in motor starting switches, commercial and aircraft relays, light duty circuit breakers, and others. These materials generally start as a silver cadmium solid solution alloy, which is internally oxidized to produce the fine dispersion of cadmium oxide in the silver. Powder metallurgy techniques, with cadmium oxide powder as a starting material are employed to make a small percentage of these composites. The most popular composition is the 10% cadmium oxide version, with others ranging from 5% to 15%. Some alloys of silver-copper-cadmium-nickel are also used in contact applications ranging from 5% to 25% cadmium. It is believed that consumption is in the range of 50,000 pounds cadmium annually. The market for this material is expected to grow 4% to 5% a year, at least through 1973.

C. Silver Brazing Alloys

Many of the popular silver-base brazing alloys used in the contact industry, and other facets of the electrical and electronics markets, contain cadmium in the range of 5% to 95%, and probably averaging 18% to 20%. Looking at figures presented in "Silver-Economics Metallurgy and Use", by Butts and Coxe, and the March 1968 edition of "Mineral Industry Surveys", published by the Bureau of Mines on Silver, it appears that from 12 to 18 million troy ounces of silver currently go into the product area. If we factor the average with the expected consumption of cadmium bearing alloys and the average percent cadmium, it is estimated that consumption in silver brazing alloys is about 225,000 pounds cadmium ±15%.

D. Copper-Cadmium Alloys

Automobile radiators have historically been made of copper. Aluminum radiators offer a potential replacement for copper. Recent advances in the technology of welding or brazing of aluminum have forced a reduction in the quantity of copper used in radiators in order to remain competitive. In order to preserve mechanical stability and thermal conductivity, while reducing the mass of copper, special hard copper alloys were developed. Several alloy systems using cadmium and/or chromium are attractive. At present, Cu-Cd with 0.2% Cd is being used by several automobile manufactures in 1969 models. The total cadmium in this application is small and believed to be only 15,000 pounds. The selection of hardened copper versus aluminum will be determined by changing technology and at this time the eventual solution is not clear.

A 1% cadmium alloy is used for the manufacture of small piece parts used in the electronics industry; and it is estimated that consumption is 28,000 pounds of cadmium.

The total use of cadmium in metallurgical application is modest and amounts to about 450,000 pounds.

IV. Batteries - Cadmium

The current usage of cadmium in batteries is divided approximately 60% for sealed and 40% for vented nickel-cadmium cells. Other cadmium-containing batteries and solar cells constitute only a very small fraction of the total usage and may be neglected. At present, it is estimated that approximately 400,000 pounds of cadmium, primarily as cadmium compounds, are used in production of nickel-cadmium batteries.

Considering the growth in sealed and vented cell markets, both civilian and Government, it is estimated that annual cadmium usage in battery applications will approach 600,000 to 700,000 pounds by 1974. The ratio of sealed to vented cells should increase somewhat in this period.

In batteries, cadmium is used primarily as compounds. The 99.9 percent pure cadmium balls in the stockpile are difficult to relate directly to the purity of cadmium compounds. If it may be assumed that some purification could occur during conversion to the compounds, then the purity of the stockpile is satisfactory.

Sealed Cells: The principal uses of sealed cells are in communications, e.g., transceivers and portable telephones, in motor starting, e.g., lawn mowers and in convenience appliances, e.g., shavers. It may be anticipated that both communication and motor starting applications will increase in volume more rapidly than the appliance application unless new novelty items evolve, as did the cordless toothbrush and knife. There is also the possible increased use by the military of sealed nickel-cadmium batteries as a power source for field missile systems, etc. Although nickel-cadmium batteries are used extensively in space applications, this use constitutes only a small fraction of the total volume.

Vented Cells: The principal uses of vented cells are in airplaines, helicopters, and special military applications. These applications should grow primarily with an expected increase in aviation applications.

An uncertain factor in the future is electric vehicle propulsion, especially hybrid systems using batteries as a surge power source and fuel cells or small gasoline engines for steady power. The electric car is so closely connected with air pollution control with its political overtones that projections are difficult. Although experimental or prototype cars may be available in five years, this application is not considered to be significant for the next five years.

V. Cadmium Compounds

Consumption of cadmium for production of compounds, including pigments, accounts for approximately 40% of total cadmium demand. The starting material for compounds is cadmium metal, either in refined shapes or as sponge. However, certain cadmium compounds, most notably the oxide, are an intermediate step in many of the production processes.

Most important of the compounds are pigments accounting for 2,457,000 pounds of total cadmium consumption. The cadmium sulfide-based pigments occur in a wide range of yellows (ZnS-CdS), oranges (CdSe-CdS), and reds (CdSe-CdS and HgS-CdS), with outstanding properties of high color absorption coefficient; finely divided (submicron) form; stability to heat, light, moisture, weathering, and various chemicals; low solubility in water and in the solvents and vehicles used in pigment applications; and reasonable cost. These pigments have attained wide commercial applications in plastics, paints, enamels, lacquers, and printing inks.

An important and growing use of cadmium is as a vinyl stabalizer, both to provide stability during processing and to prevent degradation of the end-product when exposed to light. The cadmium may be added as a soap with such fatty acids as stearic acid, with a non-fatty acid such as benzoate, or as organic phosphites.

Cadmium phosphors continue to be used in significant quantities for black and white television tubes. The original application of cadmium phosphors for the red component of color TV has apparently been almost completely replaced by a europium-activated yttrium ortho-vanadate, but that decline has been offset by the growth of cadmium phosphors for the blue and green components. Another important use of cadmium phosphors is a coating for flourescent tubes.

The active material of the negative electrode for manufacture of a nickel-cadmium battery is normally cadmium oxide, although other cadmium compounds or the metal may be employed. In the cadmium plating process, various salts of cadmium are used for the plating bath. High-purity cadmium compounds in crystal form have been among the leading materials utilized for semiconductor photoactive and other sophisticated solid state physics purposes. Although relatively small in quantity requirements, these electronic uses represent a high value and are of strategic importance.

In summary, cadmium compounds have a widespread base of commercial application with an upward consumption trend and are considered to be probably less sensitive to small price changes than other areas of cadmium use. For compounds other than the pigments, there may be an element of double accounting since some of these compounds may be included as an end use in PVC stabilizers, battery materials, or plating salts.

VI. Thermoplastics

The addition of stabilizers to thermoplastics like polyvinyl-chloride (PVC) is necessary and, therefore, it has become a common industrial practice. These stabilizers often contain a metal salt of an organic acid, like stearic acid, for example. Cadmium salts along with barium, zinc, and aluminum salts are common stabilizers. Certain compounds of lead such as the carbonates, tri- and tetra-basic sulfate, and dibasic phosphite are also used. Tin stabilizer systems based on dibutyl thio tin, dibutyl tin laurate, and certain octyl tin esters are now used as well. Several purely organic stabilizer systems find commercial use. Cadmium salts are seldom used alone, but rather are used in combination with barium salts.

The quantity of PVC used exceeds several billion pounds annually. The fraction of the stabilizer market held by barium and cadmium is about 50%. The quantity of cadmium as metal consumed in 1968 has been variously estimated as being between 2.2 to 2.5 million pounds.

Polyvinyl-chloride containing cadmium salts as a stablilizer is a clear material and used for packaging. Sheets of the polymer material are calendered. Tin stabilizers, such as dioctyl tin maleate and dioctyl tin-bis-iso-octyl thioglycollate, have received USFDA approval for food packaging. Tin stabilizer systems are more efficient than cadmium systems and their loading in the PVC can be lower. However, despite their higher efficiency, the tin systems are more expensive per pound of PVC than systems based on cadmium. The economic trend of this situation may change as the tin market grows and experience in manufacture of the tin stabilizers grows. It is possible that the cost of tin systems could decrease to a point where they could replace, or at least supplement, cadmium in the general packaging market.

VII. Electroplating

Historically, cadmium plating has been the largest single use of the metal in both the United States and the United Kingdom. The pattern of consumption is unusual in that most platers are small and they are geographically diffuse. The composition of cadmium plating solutions is well known. Their use is usually trouble free. With the exception of brightners purchased separately, this state of affairs has freed the plater from the necessity of using proprietary solutions. As a consequence of the ease in making up and replenishing solutions rather than purchasing them from a vendor, it is difficult to analyze the activities of electroplaters. The cadmium anodes used by platers are balls and can be purchased from producers or plating suppliers. Cadmium is added to the bath by anode disolution; however, initial make-up and drag-out loss replacement can be achieved through the addition of oxide or salt. The best estimate of plating activity is that it consumes about 6 million pounds of the metal annually. This total is less than it was at one time. The reason for the net decrease is a matter of price of cadmium versus zinc (about $3/pound versus $0.20/pound).

There appears to have been very little change in recent years in the technical requirements for cadmium metal used for electroplating. The P-8-R National Stockpile Purchase Specification, dated 2 December 1963, is adequate for cadmium ball anodes for electroplating. In fact, most of the primary cadmium being produced in the U.S.A. and elsewhere has a purity considerably higher than required by this specification.

The most obvious substitute for cadmium is zinc, since zinc and cadmium are the only two metals commonly plated that protect iron and steel electrochemically. Techniques for electroplating zinc were improved markedly in the 1930's, and minor improvements continue. It has been possible for many years to plate a bright attractive coating of zinc that cannot be distinguished visually from a bright cadmium coating. Chemical surface treatment of bright zinc plate reduces the tendency for fingermarking and tarnishing to such a degree that, from the standpoint of decorative value, zinc plate is equivalent, for all practical purposes, to cadmium. When comparing coatings of equal thickness, exposed in most atmospheric environments, zinc is equal or slightly superior to cadmium in protective value.

From the standpoint of economics, the rather large difference in price between zinc and cadmium is strongly in favor of zinc. Very recently, solutions for plating bright zinc have been developed which contain little or no sodium cyanide. This further improves the economics of zinc plating, both from the standpoint of solution cost and cost of disposal of toxic cyanide wastes. Processes for cadmium plating are simpler to control than those for zinc plating, and preparation for cadmium plating is less demanding. There is little doubt that there is still much cadmium used for plating which could satisfactorily be replaced by zinc. The basic facts of economics will force this substitution as the demand and price for cadmium increase further.

There are some plating applications in which zinc is not a completely satisfactory substitute for cadmium. Plating high-carbon and high-strength steel parts in alkali-cyanide zinc solutions tends to cause hydrogen embrittlement, sometimes so severe that it cannot be completely eliminated by baking. Some cadmium-plating processes are available that greatly decrease or eliminate this tendency for embrittlement. However, a recently available method of applying a zinc coating by mechanical means ("peen plating") has largely overcome this difference between zinc and cadmium plating. The superior solderability and electrical conductivity of cadmium coatings are important in electronic applications. Electroplated tin can be soldered well, but in equal thickness it does not protect as well as cadmium. Tin-zinc alloy plate has also been suggested as a cadmium substitute but has not found widespread use. Cast and malleable iron components are difficult or even impossible to plate in conventional zinc solutions, especially in bulk or barrel plating. Such articles are easily plated with cadmium. When zinc-plated components are subjected to organic vapors and high humidity (tropical exposure), bulky white corrosion products form which can interfere with functioning of delicate mechanisms. Cadmium is superior to zinc in this respect. Zinc corrosion products cause rapid deterioration of some fabrics. The strength of steel parts that are stressed in service and that function at temperatures over 500°F (aircraft engine bolts), is undesirably affected by either a cadmium or a zinc coating. Cadmium coatings can be used in these applications up to 900°F if a nickel undercoating is applied prior to cadmium plating.

VIII. Conclusions and Recommendations

Based on the above analysis, consumption can be divided as follows:

Plating	6.0 million pounds
PVC Stabilizers	2.5 million pounds
Pigments	2.5 million pounds

Metallurgy	.5 million pounds
Batteries	.4 million pounds
Total Accounted For	11.9 million pounds

This is to be compared with an estimate of 13.2 million as the average apparent consumption. The remaining 1.3 million pounds, or 10% of consumption, are not explicitly accounted for. Some cadmium must be consumed in other unaccounted for ways. It might be possible to account for this quantity of metal if the estimate for electroplating is low by about 1 million pounds. This seems unlikely for it would mean a consumption of about 7 million pounds which would contradict the opinion that a reasonable portion of what was once cadmium plated is now plated with zinc. The most plausible judgment is that the individual estimates for the several categories are conservative, and therefore they are low, resulting in an cumulative error is about 1 million pounds.

A comparison between the results of this survey and those of the Department of Commerce survey, as given earlier in this report, is informative. If it is assumed that a large part of the tool and die category is in-shop plating, the results are less discordant. The battery area in 1965 was quite active with a number of new consumer convenience items that contained sealed cells selling quite well. A category for "stabilizers" does not appear in the Department of Commerce report; however, it seems reasonable to assume that the heading "reagents" could account for the cadmium used in this application. A large portion of the difference between the quantity of metal consumed as "stabilizers" vs. "reagents" can be rationalized by the increase in this end-use of cadmium that has taken place since 1965.

In the past few years, because of the large and unexpected growth of a new use for cadmium as a thermoplastic stabilizer, it is recommended, in order to assess the changing demands of technology, that a periodic analysis of cadmium consumption be undertaken. It is further recommended, that because of the nature of the cadmium plating industry, prior to any future survey or perhaps as a part of such a survey, an extensive analysis of cadmium consumption by the electroplating industry be undertaken. It is the opinion of the present Committee that such a survey be sponsored by a suitable arm of the Federal Government and that its conclusions be based upon the response to a formal questionnaire sent to individual corporations rather than be based on "the best judgment" of several well-informed individuals in the field.

Some general conclusions about cadmium consumption and production are possible. These remarks strongly bear on the difficulty encountered by the Committee in writing this report. Cadmium is a by-product of zinc production and, as such, its origins are diffuse and its distribution pattern to consumers is poorly defined. There is no "institute" concerned with cadmium, as there is for copper or nickel, and as such no coherent body of facts is readily available to an investigator. The uses of cadmium cross many technologies and the details of a given technology are often proprietary. In a given technology, there are several users of cadmium in common and communication presents a problem. Because of this diversity of uses, changing technology can cause consumption in a particular old or new area to exert unusual leverage in the market place since the supply of metal is relatively inelastic.

The cost of cadmium in many applications is only a small or modest fraction of the total cost of an end item; therefore, except for electroplating, large areas of use are relatively unaffected by changes in price of cadmium. Predicting a trend in this sort of situation has historically been unsuccessful. This report, therefore, contains few predictions; in the few areas where it has been possible to forsee consumption, the predictions are for relatively minor portions of the total usage. This is the background leading to the recommendation made earlier for a survey of the electroplating industry.

TABLE I

Salient Cadmium Statistics
(in millions of pounds)

	1964	1965	1966	1967	1968
U. S. Production	10.46	9.67	10.46	8.70	10.65
U. S. Consumption	9.36	10.43	14.78	11.56	13.33

TABLE II

Cadmium Consumption in the United Kingdom
(in millions of pounds)

	1967
Plating Anodes	1.08
Plating Salts	.27
Cadmium-Copper Alloys	.62
Other Alloys	.62
Batteries	.27
Solder	.14
Colors	.95
Miscellaneous	.18