ANACONDA ELECTROLYTIC WHITE LEAD

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Anaconda Electrolytic White Lead

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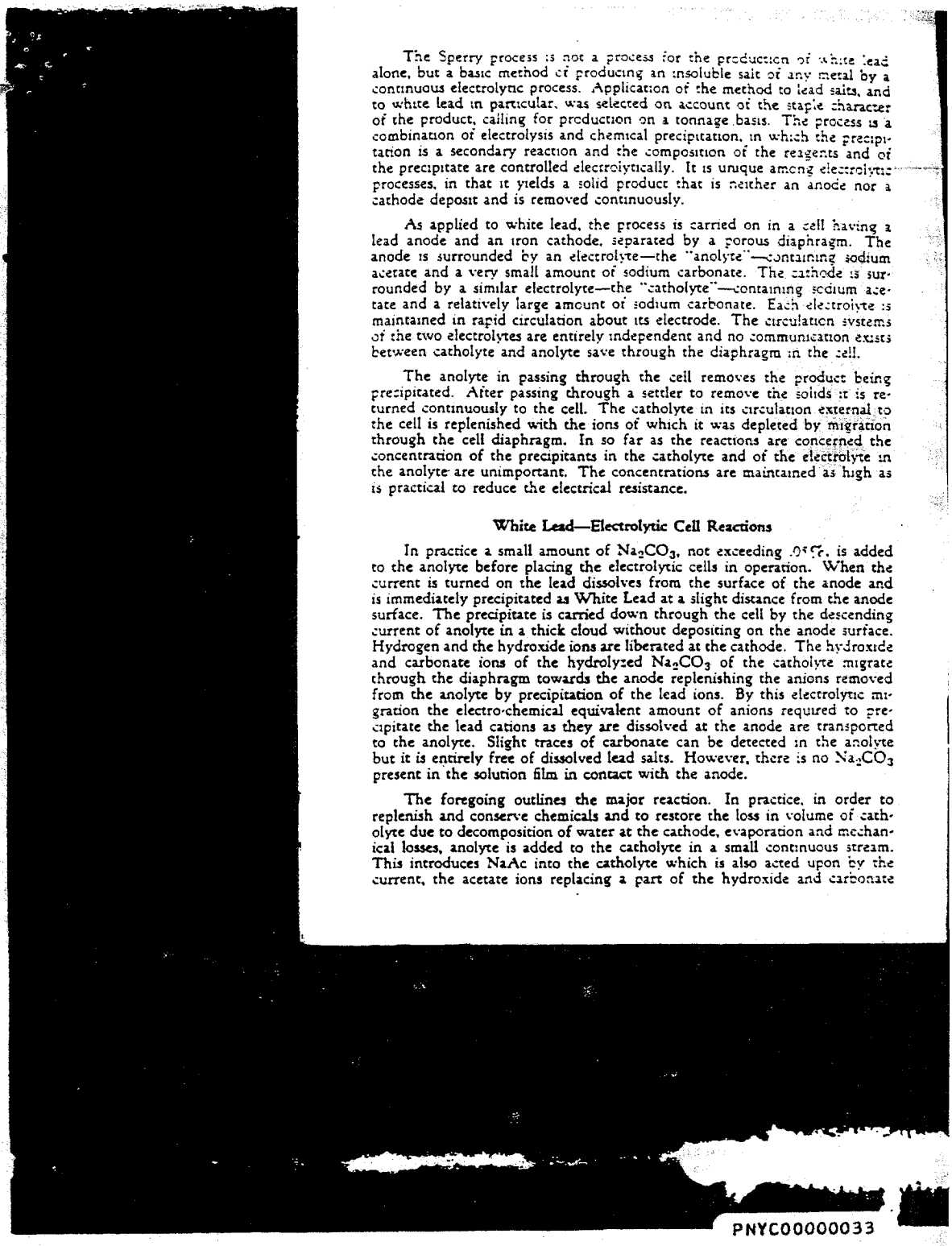
Discussions of processes for the manufacture of white lead generally open with the statement that white lead is the oldest chemical pigment known to man. This fact is of more than historical interest; in the light of the present extensive use of white lead, it indicates that the compound possesses characteristics that make it unique among white pigments, and superior to all in its particular field. A greater variety of processes have been proposed for manufacturing white lead than for any other one chemical compound. Only a few of these processes have come into commercial use, however, and a large part of the present production here and abroad is made by the process used in ancient times.

The outstanding disadvantages of the old process are that it is slow and laborious, affords no control of the product, and yields at best an impure material lacking in uniformity. Improved processes have had as their main object the shortening of the time required. Most of them accomplish this and some have yielded a superior product as well, but only two or three are now in use commercially.

For centuries the manufacture and mixing of paints has been treated as an art, and the practice has been much influenced by tradition and precedent. There is a reluctance to abandon old materials for this purpose; the quaint clumsiness of the ancient methods of manufacture has long been credited with imparting to the product a homespun quality of purity and integrity, and the adoption of the modern processes has been slow. The electrolytic production of white lead is not new, a large number of processes and forms of apparatus have been proposed and patented within the 25 years preceding the introduction of the Sperry process, all directed toward the production of white lead, wholly or in part, by electrolysis. One or two of these processes were tried commercially but proved unsuccessful.

Process

The Sperry process, used by the Anaconda Lead Products Co., is the invention of Elmer A. Sperry, and was worked out to a commercial basis at the East Chicago plant. It resembles, in a general way, earlier methods but embodies the features that make it possible to operate continuously and to produce a uniform product, the character and composition of which are under complete control. It has made possible the rapid production of white lead of a degree of chemical purity and brilliant "whiteness" superior to any produced by other methods. These properties of the product are independent of the purity of the metallic lead used.



The Sperry process is not a process for the production of white lead alone, but a basic method of producing an insoluble salt of any metal by a continuous electrolytic process. Application of the method to lead salts, and to white lead in particular, was selected on account of the staple character of the product, calling for production on a tonnage basis. The process is a combination of electrolysis and chemical precipitation, in which the precipitation is a secondary reaction and the composition of the reagents and of the precipitate are controlled electrolytically. It is unique among electrolytic processes, in that it yields a solid product that is neither an anode nor a cathode deposit and is removed continuously.

As applied to white lead, the process is carried on in a cell having a lead anode and an iron cathode, separated by a porous diaphragm. The anode is surrounded by an electrolyte—the "anolyte"—containing sodium acetate and a very small amount of sodium carbonate. The cathode is surrounded by a similar electrolyte—the "catholyte"—containing sodium acetate and a relatively large amount of sodium carbonate. Each electrolyte is maintained in rapid circulation about its electrode. The circulation systems of the two electrolytes are entirely independent and no communication exists between catholyte and anolyte save through the diaphragm in the cell.

The anolyte in passing through the cell removes the product being precipitated. After passing through a settler to remove the solids it is returned continuously to the cell. The catholyte in its circulation external to the cell is replenished with the ions of which it was depleted by migration through the cell diaphragm. In so far as the reactions are concerned the concentration of the precipitants in the catholyte and of the electrolyte in the anolyte are unimportant. The concentrations are maintained as high as is practical to reduce the electrical resistance.

White Lead—Electrolytic Cell Reactions

In practice a small amount of Na_2CO_3, not exceeding .05%, is added to the anolyte before placing the electrolytic cells in operation. When the current is turned on the lead dissolves from the surface of the anode and is immediately precipitated as White Lead at a slight distance from the anode surface. The precipitate is carried down through the cell by the descending current of anolyte in a thick cloud without depositing on the anode surface. Hydrogen and the hydroxide ions are liberated at the cathode. The hydroxide and carbonate ions of the hydrolyzed Na_2CO_3 of the catholyte migrate through the diaphragm towards the anode replenishing the anions removed from the anolyte by precipitation of the lead ions. By this electrolytic migration the electro-chemical equivalent amount of anions required to precipitate the lead cations as they are dissolved at the anode are transported to the anolyte. Slight traces of carbonate can be detected in the anolyte but it is entirely free of dissolved lead salts. However, there is no Na_2CO_3 present in the solution film in contact with the anode.

The foregoing outlines the major reaction. In practice, in order to replenish and conserve chemicals and to restore the loss in volume of catholyte due to decomposition of water at the cathode, evaporation and mechanical losses, anolyte is added to the catholyte in a small continuous stream. This introduces NaAc into the catholyte which is also acted upon by the current, the acetate ions replacing a part of the hydroxide and carbonate

ions that migrate to the anolyte. This is compensated for by permitting a certain amount of seepage of catholyte into anolyte through the diaphragm. The seepage is controlled by selecting a diaphragm fabric of the desired porosity for a given hydrostatic solution head of catholyte in the cathode compartment. The addition of relatively small amounts of anolyte to catholyte and catholyte to anolyte permits adjusting the sodium concentration of the two electrolytes and the conservation of chemicals, since all make-up solution can then be added to the anolyte in the form of filtrate from the filters. All anolyte in the filter cakes is replaced by water by a counter current washing operation and returned to the anolyte circulation system. In addition wash water filtrate is also returned as required to replenish the losses enumerated above. As the volume of solutions transferred between the two electrolytes is very small the anolyte as previously stated is essentially free of the reacting salts and they are only brought into the zone where the white lead is precipitated in electro-chemical equivalent amounts, there is never an excess present to alter the reaction or influence the size of the particle.

The White Lead which is removed continuously from the cell by the circulation of the anolyte, is removed from the anolyte by settling and filtering. The filter pulp is washed, dried, ground and air floated, and is then barrelled in a dry pulverulent form. The clear anolyte is recirculated through the cell.

The composition of the anolyte during its passage through the cell remains unchanged except for a small increase in the acetate concentration. This is controlled by dilution with wash water from the filter. The catholyte is depleted in carbonate ions and a small percent of acetate ions, and enriched in hydroxide ions during its passage through the cathode compartment of the cell. The excess of hydrate ions is neutralized and the loss in carbonate ions restored by passing the catholyte through carbonation towers, in which a stream of descending solution passes through a rising stream of CO_2 gas from a coke burning boiler. The acetate loss is replenished as noted by running a small stream of anolyte into the catholyte after it is discharged from the cells.

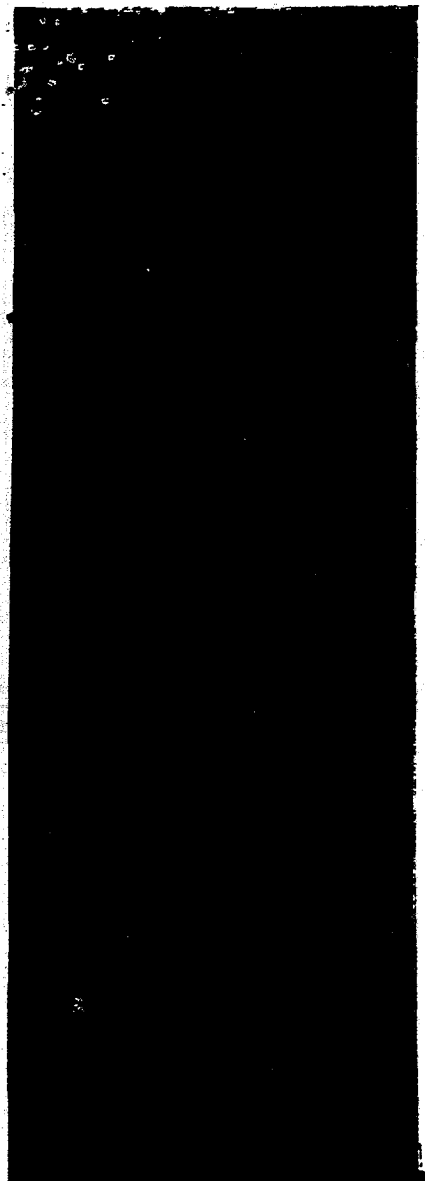
White lead is a basic carbonate of lead. The actual composition of the compound may therefore be varied. When a solution of a carbonate salt is added to a solution containing a soluble lead salt and White Lead is precipitated the empirical equation for the reaction that takes place in the formation of White Lead of theoretical composition is generally given as:

$$3\ Pb(C_2H_3O_2)_2 + 2\ Na_2CO_3 + 2\ NaOH = 2\ PbCO_3 \cdot Pb(OH)_2 + 6\ NaC_2H_3O_2$$

The composition of the electrolytic cell solution would indicate that the equation should be written:

$$3\ Pb(C_2H_3O_2)_2 + 4\ Na_2CO_3 + 2\ H_2O = 2\ PbCO_3 \cdot Pb(OH)_2 + 2\ NaHCO_3 + 6\ NaC_2H_3O_2$$

Since analysis of the anolyte of the electro-chemical cell shows that $NaHCO_3$ is produced at the time that White Lead is precipitated, the re-



action indicated, therefore, is that the Na_2CO_3 is hydrolyzed to form $NaHCO_3$ and NaOH, and that the intermediate compounds $Pb(CO_3H)_2$ and $Pb(OH)_2$ are first formed, which in turn react to produce the compound $Pb(CO_3PbOH)_2$. This formula is preferred as it indicates the formation of a compound and not a mixture, as $2\ PbCO_3 \cdot Pb(OH)_2$ would indicate.

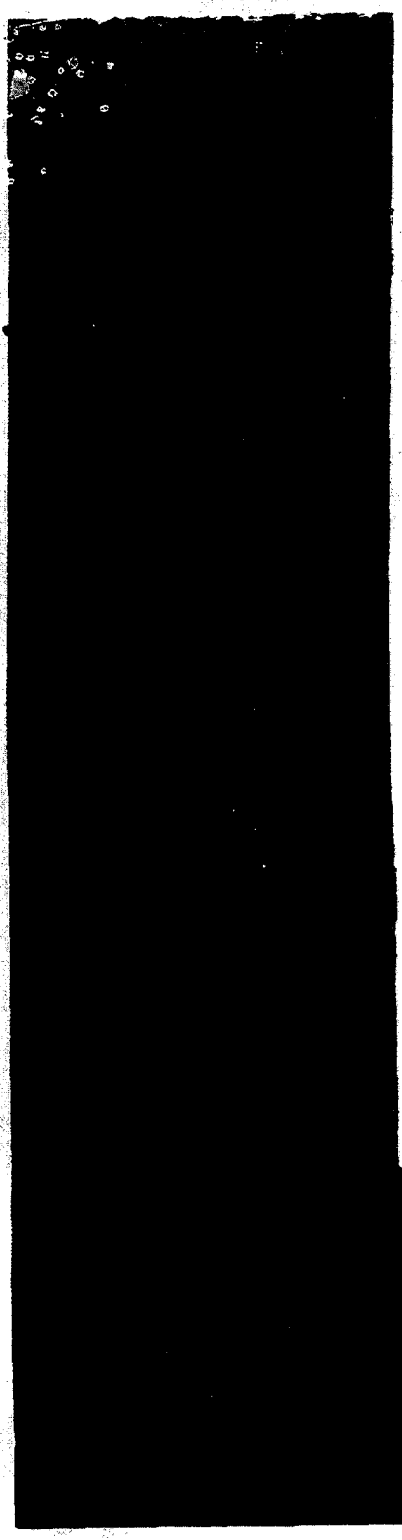
Characteristics of Product

The outstanding characteristics of the White Lead produced by the electrolytic process are exceptional purity, brilliant whiteness, and uniformity.

The exceptional purity and freedom from contamination are the results of the initial exclusion from the white lead of all metallic impurities contained in the original lead, exclusion of the impurities in the chemicals employed and the elimination of all external sources of contamination. The metallic lead undergoes a refining action in the electrolytic cell, only lead being dissolved. The metallic impurities commonly found in lead, such as bismuth, antimony, and silver, together with small particles of unconverted lead, remain as a firmly adhering slime on the surface of the anode. Other impurities that could be introduced with the other raw materials used are excluded by adding these raw materials to the catholyte; the fabric diaphragm, which separates this solution from the solution in which the white lead is formed, is an efficient filter. Water soluble salts are removed by washing the product with hot water. There is no soluble basic lead acetate present and the washed product is neutral or slightly alkaline. Proper selection of materials of construction and the exclusion of atmospheric dust have brought about the elimination of the third source of contamination. The brilliant whiteness is the result of the exceptional purity thus obtained.

The characteristic uniformity of the physical and chemical properties of this white lead and the ease with which these properties can be varied are the result of the positive control of the chemical reactions taking place in the electrolytic cell. Automatic recording and regulating instruments are used throughout the plant to insure complete records, to permit control of all operations, and to maintain uniform operating conditions. There is practically no variation in any of the operating factors, such as chemical composition of the electrolytes, current density, temperature of solutions, or rate of flow of solutions. The product is the true basic carbonate which is usually given the formula $2\ PbCO_3 \cdot Pb(OH)_2$ in text books, more probably $Pb(CO_3 \cdot PbOH)_2$ since it is a single compound and not a mixture as the older formula would suggest.

The physical properties of electrolytic white lead can be varied over rather a wide range to meet changing specifications. This is accomplished by changing the operating constants of the cell. Following is a tabulation showing the range over which the physical properties are varied in producing the various grades of electrolytic white lead now marketed. In some cases these figures are not strictly comparable with other published figures.



as the method of making the determination may vary or a common standard for comparison may be necessary.

Relative Range in Physical Properties of Various Grades of Electrolytic White Lead

Flow (Gardner Flowmeter)* 34.6% Oil—65.4% Pigment, ... 2.35 to 3.77 inches
Oil Absorption. (Gardner-Coleman), per 100 gms. ..... 11.75 to 19.45 cc
Oil Absorption. (Standard Rubout Method), per 100 gms., ... 8.35 to 14.33 gms
Hiding Power. (Pfund Cryptometer), per pound..... 13.60 to 25.30 sq. ft.
Tinting Strength (Ultramarine), DuPont Numerical Strength Scale ..... 75% to 131%
Particle size. Weighted average..... .95 to 1.54 microns

*Refined linseed oil, acid number 5, is used.

Miscellaneous Data—Electrolytic White Lead

Brightness	Blue	Green	Red
Pfund Colorimeter	(480 uu.)	(490 uu.)	(630 uu.)
Percent Diffused Reflection	87.4	89.2	89.8
Specific Gravity			6.81
Residue on 325 mesh			0.10%
Insoluble			0.01%
Free Acetic Acid			None
Moisture			0.25%
Wt. per Solid Gallon			56.73 Lbs.
One Pound Bulks—Gallons			0.01763

Bibliography

The development of the Sperry electrolytic white lead process has created much interest in the paint industry and among electrochemists. Several descriptive articles have been published and are listed below. The above description represents a consolidation of material from a number of these articles, with some additions to bring the whole up to date.

"Anaconda Electrolytic White Lead," by R. G. Bowman. Transactions A. I. M. E. Vol. 73, 1926, pp. 146-170.

"Electrolytic White Lead," Paint, Oil & Chemical Review, Chicago. August 25, 1927.

"Pioneer Work in Development of White Lead Manufacture by Sperry Electrolytic Process," by R. G. Bowman. Engineering & Mining Journal, Vol. 128, No. 8, page 318.

"Electrolytic White Lead," by W. J. Knox. Paint & Varnish Production Manager, Vol. 34, No. 5, November, 1929, pp. 22-24.

"The Manufacture of Electrolytic White Lead," by I. G. Katz. The Armour Engineer, Vol. 21, No. 3, March, 1930, pp. 88, 89, 116.