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FIG. 1.—CONVEYING TAN-BARK.— ENGLISH MANUFACTURE
OF WHITE LEAD.

THE LEAD AND ZINC PIGMENTS

BY
CLIFFORD DYER HOLLEY, M.S., PH.D.

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FIRST THOUSAND

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INTRODUCTION.

POSSIBLY in no other country has the art of pigment and paint making reached as high a level as in the United States. Certainly in no other country has the paint industry developed as rapidly during the last forty years as it has in America. The making of one hundred and fifty thousand tons of lead pigments and over seventy thousand tons of zinc pigments, resulting in the manufacture of over one hundred million gallons of paint besides the enormous sales of lead in oil, constitutes an industry that is to be counted among the important industries of the country. And yet until the passage of the first efficient and vigorous paint law in 1905, enacted by the state of North Dakota, and the court proceedings attendant thereto for the determining of the constitutionality of that law, those interested in the subject of pigments and paints were compelled to turn to English books for information, as our own literature was noticeable only for its meagerness.

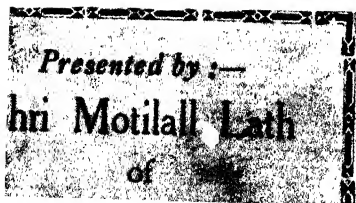
New pigments have come into use during the last ten years, new processes have been developed for the manufacture of the older pigments, new combinations of pigments have been worked out that have secured results hitherto unattainable. Yet up to the time mentioned above, except for short articles in some of the trade papers, these improvements and innovations remained practically unnoticed. Since public attention has been directed to the paint industry by the enactment of the various state laws regarding the sale of paint materials, several excellent

American works have been written on this subject, but the majority of them have been directed more particularly toward the compiling of analytical methods and data than to the manufacture and uses of the various pigments.

In this work the author has attempted to record the progress made in the United States in the manufacture of the more important pigments, and hence but little space has been given to European methods and processes except for comparison, as they have been discussed in detail in various English and European works.

The writer wishes to express his appreciation for the valuable information and data furnished him by Mr. Willson H. Rowley, who for many years has been prominently identified with the white lead industry and who has done much to place it on a more sanitary, scientific, and economical basis.

DETROIT, MICH., July 1, 1908.



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THE LEAD AND ZINC PIGMENTS.

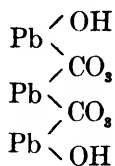
CHAPTER I.

WHITE LEAD IN ANCIENT TIMES.

1. **Importance of White Lead Industry.** The lead products industries are to be reckoned among the most important industries of the country. Of the 331,000 tons of lead produced in 1907, it is estimated that over 135,000 tons were used in the manufacture of white lead, red lead and litharge, an amount equivalent to over 40 per cent of the entire lead consumption. The conversion of this amount of metal into chemical products represents a large outlay of capital and the employment of a large number of workmen, in the nearly fifty plants producing these pigments in the United States. The production of litharge and red lead is small, however, as compared with white lead, which required during the year referred to about 100,000 tons of metallic lead.

2. **Composition.** White lead is perhaps the best known of all the white pigments and has been in general use from very ancient times. Chemically white lead is a basic carbonate of lead. A large number of analyses of the best samples indicate a constitutional formula of $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, in which there are two molecules or equivalents of lead carbonate to one of hydroxide, the

combination being represented by the following structural formula:



White lead may be made to vary a good deal in composition according to the method and conditions of making, and many writers in comparing the more modern pigments, such as sublimed white lead and zinc-lead white, with white lead have commented much on these variations; but white lead as manufactured to-day, whether by the Old Dutch process or by the quick processes that have been found by experience to be economically successful, varies but comparatively little in composition as regards the ratio of carbonate to hydroxide.

3. Historical. White lead was known to the ancients under the Greek name of *psmithium* and the Roman name of *cerussa*. Perhaps the earliest definite and reliable account of its manufacture is given in Theophrastus' "History of Stones," written about 300 years before Christ, in which the author describes the method of manufacture substantially as follows:

"Lead is placed in earthen vessels over sharp vinegar, and after it has acquired some thickness of a sort of rust, which it commonly does in about ten days, they open the vessels and scrape it off, as it were, in a sort of foulness; they then place the lead over vinegar again, repeating over and over again the same method of scraping it till it has wholly dissolved. What has been scraped off they then beat to powder and boil for a long time, and what at last subsides to the bottom of the vessel is ceruse."¹

¹ Theophrastus, *History of Stones*, p. 223.

4. Vitruvius, writing in the first century before Christ, says: "It will be proper to explain in what manner white lead is made. The Rhodians place in the bottom of large vessels a layer of vine twigs, over which they pour vinegar, and on the twigs they lay masses of lead. The vessels are covered to prevent evaporation, and when, after a certain time, they are opened the masses are found changed into white lead."¹

5. Pliny, the historian, living in the first century A.D., mentions a native ceruse (cerussite) found in Smyrna which the ancients made use of for painting their ships, but adds that "all ceruse is prepared from lead and vinegar,"² and the most esteemed, he adds, comes from Rhodes.

These and other descriptions by the ancient writers and historians can only be regarded as imperfect and crude statements of processes they personally knew little or nothing about, and it is natural that their descriptions should be lacking in many essential details. Their methods if followed exactly as described would produce only lead acetate, which, besides being very soluble in water, possesses but little opacity or hiding power.

6. Essential Conditions for Manufacture of White Lead. Three conditions are essential for the proper manufacture of white lead from metallic lead and vinegar or acetic acid:

1. The placing of the lead above the acid so that it would not come in contact with it.
2. A long continued gentle heat, such as would be obtained by the use of horse manure or by the fermentation of moist tan-bark.
3. The presence of carbon dioxide in considerable quantities.

¹ Vitruvius, p. 186.

² Pliny, *Natural History*, Book XXXV, Chap. IX.

7. That the ancients were well acquainted with the first requisite is evidenced by the descriptions already given. Pliny also in describing the manufacture of white lead says, "It is made from very fine shavings of lead placed over a vessel filled with the strongest vinegar."¹

Discorides, writing in the first or second century, states: "Having poured vinegar . . . into a broad-mouthed pitcher, or an earthen jar, fasten firmly a mass of lead near the top of the jar upon a mat of reeds previously stretched beneath."²

In another place he explains more in detail, "Having suspended a stick of wood about the middle of the jar, place the mat of twigs before mentioned upon it, in such a manner that it may not touch the vinegar."

8. The second requirement, that of a gentle but long continued source of heat, while not mentioned by some of the earlier writers, is specifically mentioned by at least two. Discorides states that the manufacture of white lead can be carried on in the winter as well as in the summer, "if you place the jar over braziers, cauldrons or furnaces; for heat applied to it shows the same effect as the sun," thus indicating that advantage was taken of the sun's rays as a source of heat. Galen, writing in the second century, says that white lead is made by dissolving litharge in vinegar, burying the vase containing these substances in dung for forty days.³ Here we also have a probable source of heat mentioned.

9. In regard to carbon dioxide, the third requisite necessary for the proper manufacture of white lead, it can be said that none of the ancient writers mention any means of securing its presence or in any way indicate that

¹ Pliny, *Natural History*, Book XXXIV, Chap. LIV.

² Discorides, *De Materia Medica*.

³ Hoffmann, *Das Blei*, p. 42.

carbon dioxide or any gas was necessary for the preparation of ceruse. This omission on their part has led some modern writers to doubt that the ancients were acquainted with what we know as white lead. However, if we consider the exceedingly imperfect knowledge that the ancients had regarding the chemistry of the various processes they used in their manufactures, this omission is not to be wondered at, especially when we consider the impure nature of the vinegar or acetic acid in use in early times, due to the crude and imperfect methods of manufacture, which necessarily resulted in a considerable amount of grape skins and pulp passing into the expressed juice. These impurities naturally evolved considerable carbon dioxide in the course of their decomposition, an amount sufficient at least to carbonate a considerable quantity of lead. This method of producing carbon dioxide being so closely associated with the natural fermentation of the grape juice into vinegar, might well pass unnoticed and uncommented upon by the ancient experimenters and historians. In support of this contention, Pulsifer cites the following statement from Gentele's *Lehrbuch der Farbenfabrikation* regarding the modern manufacture of white lead at Klagenfurth, in Carinthia: "The acetic acid and the carbon dioxide being simultaneously produced by the fermentation of the extract of dried grapes or raisins, or of the residuum of grapes after pressing. Water-tight boxes are prepared into which the raisins or the residuum is placed; to this is added a quantity of vinegar. When subjected to heat, the vinous fermentation begins in the sweetish liquor, producing alcohol and carbon dioxide, and the acetic fermentation also occurs in the alcohol, producing acetic acid."

Viewing the matter in this light, the presence of carbon dioxide can be satisfactorily accounted for in the processes

used by the ancients, and the product obtained by them was a true white lead, although probably badly contaminated with both the normal and the almost insoluble basic lead acetates.

It is quite certain that white lead was made in notable quantities at the beginning of the Christian era. According to the historians, Rhodes was the most important seat of manufacture, although the industry was sufficiently notable in Corinth and Lacedaemonia to be mentioned by Pliny.

10. Early Improvements. Little practical advancement was made in the art of making white lead for many hundred years after the beginning of the Christian era. This is not to be wondered at when we consider the decay of learning and the dismemberment of the Roman Empire. Such knowledge as survived was locked up in the various monasteries, and it is to the various manuscripts written by the monks that we must look for our information. Many of the references that have been found regarding methods or recipes for the manufacture of white lead were evidently copied from still earlier writings, which in turn may have been and in fact probably were, taken from the manuscripts of the Greek and Roman historians already referred to. Some of the manuscripts, however, seem to be more than copies and really serve as a connecting link between the methods used by the ancients and those in use at the present time, and indicate certain noteworthy improvements in the art. Especially are the writings of Theophilus and Eraclius of interest, as they imply that decomposing horse dung came into use during this period as a source of gentle heat for carrying the reaction through to completion and also unwittingly perhaps as a source of carbon dioxide gas. Also both writers mention the use of linseed oil as a vehicle for preparing paints. Theophi-

lus in particular gave elaborate directions for the preparation of linseed oil and the grinding of white lead in oil.

11. **Effect of the Revival of Learning.** The revival of learning in Europe, beginning in the eleventh century, was accompanied by a renewed activity in manufactures and scientific pursuits, and the manufacture and use of white lead became an item of importance throughout western Europe and Great Britain, although its use was confined almost entirely to paintings and church decorations. History relates that the chapel of Saint Stephen in England was rebuilt in 1352 and that all of the painters in the surrounding country were employed in its decoration. Among the items for material were the following:¹

	£	s	d
19 pounds white lead for priming at 4 <i>d</i>	0	6	4
4 flagons of painter's oil.....	0	16	0
62 pounds red lead at 5 <i>d</i>	1	5	10
$\frac{1}{2}$ pound red lead.....			8

And again:

Item: To John Lightgrave

	£	s	d
51 pounds white lead at 2 $\frac{1}{2}$ <i>d</i>	0	10	7 $\frac{1}{2}$
53 pounds white lead at 3 $\frac{1}{2}$ <i>d</i>	0	15	5
43 pounds red lead at 4 <i>d</i>	0	16	6
3 pounds white lead.....	0	1	0

The considerable variations in price might indicate that the use of reduced or adulterated white lead was by no means uncommon even at that time, a fact which was severely commented upon by various writers at a slightly later date.

12. The methods of manufacture described in the various authentic documents of the period, while indicating that the

¹ Pulsifer, *History of Lead*, p. 243.

manufacture was carried on on a more extended scale and with a continual improvement in technical knowledge, still followed closely the principles recorded by Vitruvius, Pliny, Theophilus, and others, except that the advantages resulting from the use of stable manure as a source of heat were now fully recognized.

13. Development of the Lead Industry by the Dutch. It is almost universally believed that the Dutch were the inventors or originators of the process of manufacturing white lead by which the larger part of our white lead is made to-day, viz., the "Dutch process," the usual date given for the establishing of the industry in Holland being 1622. As has been clearly shown, however, the industry did not originate with the Dutch, but was in general use throughout western Europe prior to that date; in fact, as Pulsifer points out in his "History of Lead," that "the description in the manuscript of Theophilus varies in no important particular from that used by the Dutch in the seventeenth century, even to the use of stable litter. Objection may be made to the statement that Theophilus did not secure the necessary carbon dioxide from the decomposing dung, neither did the Dutch in the seventeenth century depend upon the decomposition of the ferment for this element, but added to the vinegar in the pots wine lees, bits of marble, and other substances capable of producing this necessary factor."

He states further in the same connection, "it is impossible, therefore, that the Dutch invented a process which is clearly described in manuscripts written before the foundation of Amsterdam, and it is unlikely that they borrowed from the Arabs in Spain a method which had been practiced for more than three hundred years in the Italian cities with which their neighbors, the Flemings, had been in constant communication."

14. Early Adulteration of White Lead. Nevertheless credit must be given the Dutch for developing the industry along broad commercial lines. In fact their very eagerness to monopolize the white lead industry of Europe and undersell their competitors, especially the Venetians, undoubtedly led them to adulterate their products with chalk and similar materials, to the detriment of the entire industry. Zedler in his Lexicon states "that the painter bought the Holland ceruse because it was cheaper, but contained much chalk, whereas the Venetian was pure, of great enduring qualities, and kept white until the last." Pomet, chief druggist to the French king, Louis XIV, in his complete "History of Drugs," says that they "used little else in France than ceruse de Holland, which was cheaper, and was much esteemed by the painter, but in this they were wrong, as the Dutch ceruse had so much chalk in it that it was of no long duration."

15. Von Justi, writing in 1758, states, "white lead is in much greater demand than one would suppose; the manufacture is not enough to supply the demand in this Prussian kingdom. It is best not to falsify white lead, but to prepare it pure. In Holland and England we find that a good proportion of chalk is added, and so we have been obliged to do this that we may sell it at the same price. Only the Venetian is wholly pure and on that account it is much sought after and is sold at a higher price."

16. Manufacture of White Lead in Seventeenth Century. Sir Philiberto Vernatti, writing in 1678, describes with much skill and accuracy the process used by the Venetians at that time for making white lead. His description indicates that they had reached a high state of skill in the art, such as could only have been obtained by many years of intelligent and continued activity in the industry, and which should be conclusive evidence that they were well versed

in the manufacture of white lead prior to the date ascribed to the Dutch. It is also to be noted that Vernatti's description differs in no important detail from the process now known as the Dutch process. He says: "First, pigs of clean and soft lead are cast into thin plates a yard long, six inches wide, and to the thickness of the back of a knife. These are rolled with some art round, but so as the surfaces nowhere meet to touch, for where they do, no ceruse grows. Thus rolled, they are put each in a pot just capable to hold one, up-held by a little bar from the bottom, that it comes not to touch the vinegar which is put into each pot to effect the corrosion. Next a square bed is made of new horse-dung, so big as to hold twenty pots abreast and to make up the number four hundred in one bed. Then each pot is covered with a plate of lead, and lastly all with boards, as close as conveniently can be. This repeated four times makes one 'heap' so called, containing sixteen hundred pots. After three weeks the pots are taken up, the plates unrolled, laid upon a board, and beaten with battledoors till all the flakes come off, which if good, prove thick, hard and weighty; if otherwise, fuzzy and light, or sometimes black and burned if the dung prove not well ordered; and sometimes there will be none. From the beating table the flakes are carried to the mill, and with water ground between mill-stones until they be brought to an almost impalpable fineness; after which it is moulded into small parcels and exposed to the sun to dry until it be hard, and so fit for use."

17. "Accidents to the work are; that two pots alike ordered, and set one by the other, without any possible distinction of advantage, shall yield, the one thick and good flakes, the other few and small or none, which happeneth in greater quantities, even over whole beds sometimes. Sometimes the pots are taken up all dry and so sometimes prove best; sometimes again they are taken up wet.

Whether this arises from the vapors coming from below, or by the moisture that is squeezed out by the weight of the pots, we cannot discover. This we observe, that the plates which cover the pots yield better and thicker flakes than do the rolls within; and the outsides next the planks, bigger and better than the insides."

18. The Dutch Method of Manufacture. The above description indicates that the Venetians were cognizant of the same obstacles and drawbacks that confront the corroder to-day, and that the above method is very closely similar to the Dutch process as described by the Dutch writer, Jars, approximately one hundred years later. Jars is accredited as a most careful and intelligent observer, and his statements as given by Pulsifer,¹ probably represented very closely the methods followed by the Dutch at that time.

"The lead was first cast in thin sheets which were rolled in a spiral and placed in earthen pots, seven to eight inches high and four to five inches in diameter, made wider at the top than at the bottom. To prevent the lead from falling to the bottom, they placed inside the pot, and at about one-third of its depth, a piece of wood, cut the length of the diameter of the pot. This was the Rotterdam method. At Amsterdam, the manufacturers had moulded in the inside of the pot, and at about one-third its height, three little points which served, instead of wood, to support the lead. The stacks were built in one range of four, each being about fifteen feet square. After the pots had been filled up to an indicated point with vinegar, and the spiral of lead placed in position in each pot, they were arranged in rows in the stack upon a bed of dung, four feet thick; the pots were placed together as closely as possible, and when the bed was covered with the pots, plates of lead were

¹ Pulsifer, *History of Lead*, p. 267.

laid upon them and the whole covered with boards. These boards were then covered with dung, and another tier of pots placed as before, filled with vinegar and lead, and covered in the same manner. This was repeated until five tiers, or layers, were built up. The lead was left in the stacks from four to five weeks according to the season and the quality of the dung. In one of the layers which Jars saw opened, he remarked that the action did not appear to be equally satisfactory. In some the sheets of lead were entirely corroded, in others the operation was partial only, while in a few the surface of the sheets was only slightly attacked. This unequal action he attributed to the dung heating more in some parts than in others. The sheets covering the pots formed a crust or scale, harder and more compact, and were put to one side to be used in the manufacture of *blanc de plomb*. When the dung had been used several times, it was replaced by new; that rejected was sold to be used as a fertilizer. The sheets which were partially converted were taken from the pots and placed upon heavy tables, and beaten with mallets to separate the white lead from the unconverted, care being taken to sprinkle it with water from time to time to abate the dust. The ceruse was now removed to the mills where in Amsterdam it was twice, and in Rotterdam three times ground in water, the mills being placed one above another, the lead falling from the upper mill directly to the one below it, finally passing to a tub placed below to receive it.

19. "The workmen having in charge the grinding of the lead fed the ceruse from the tubs with a ladle into the eye of the stone, adding from time to time chalk in desired proportions to form the mixture. This mixture formed the ceruse. The *blanc de plomb*, which was white lead, was ground without the admixture of any substance, and being harder and requiring to be finer and ground with

more care, the mills could produce but ten quintals per day, while of the ceruse fifteen quintals were turned out.

“The last operation, drying, was managed as follows: the ceruse in a pulpy state was filled into unglazed earthen pots, in shape like a section of an inverted cone; these pots were placed upon long wooden shelves, in a long and narrow building, in the sides of which a great number of doors were provided to open and close at pleasure, to shield the ceruse from sun and rain which would impair its color. After five or six weeks the pots were removed, and the ceruse was turned out, the contents of each pot forming a conical mass or loaf; when perfectly dry this was trimmed, tied up in blue paper and packed in barrels for market.”

20. English Method of Manufacture. The methods employed for the manufacture of white lead in England were substantially the same as those in use in Holland. In 1787, however, one Richard Fishwick obtained a patent for the use of spent tan-bark in the place of stable manure, claiming that the tan-bark communicated a more equable and uniform degree of heat to the lead and vinegar. This date undoubtedly approximately marks the introduction of this important improvement which may be considered the link connecting these earlier methods with the Dutch process as conducted to-day.

CHAPTER II.

DEVELOPMENT OF THE WHITE LEAD INDUSTRY IN THE UNITED STATES.

21. **Early Use of White Lead.** Pulsifer in his "History of Lead"¹ clearly explains the attitude of the early American colonists toward the use of white lead and of paints in general.

"There was but little need for the establishment of white-lead factories in the United States until after the Revolution. The simple habits of the first settlers, their poverty and their struggles for subsistence prohibited the use of paints for decorative purposes, while the abundance of timber rendered it unnecessary to be at any great expense to preserve it from the destructive action of the elements. The use of paint, therefore, was discouraged by the early settlers. Bishop relates the case of the Rev. Thomas Allen, of Charlestown, near Boston, who was 'called to account' in 1639 for having paint about his dwelling. The reverend gentleman secured immunity from correction by assuring the authorities of his condemnation of the practice of using paint, and by proving that the offensive substance had been applied by a former proprietor, and was there when he took possession of the premises.

22. "The dwellings of the early settlers were generally of wood, unpainted on the outside and inside. The interior walls were occasionally whitewashed, but beyond this no decoration was to be observed. The first church in Boston (destroyed by fire in 1711) was never painted,

¹ Page 313.

it is said, inside or outside. In 1705, according to Bishop, the coat of arms of Queen Anne, in the Court House at Salem, Mass., was ordered to receive a 'coloured covering,' which is said to be the first reference to art in that quarter. A list of mechanics made in 1670, in Massachusetts, fails to show the name of a single painter. Painters' colors, however, were for sale in Boston in 1714."

23. The First White Lead Plant. It is not surprising, therefore, that the development of the white lead industry was delayed for a great many years after numerous other industries had secured a foothold in the colonies. Even the actual date of the establishment of the first white lead plant is uncertain. Credit for the introduction of the industry into this country is ascribed to Samuel Wetherill & Sons, who in 1777 or shortly after had established a factory in Philadelphia for the manufacture of chemical products and were known as importers and dealers in dye-stuffs, various chemicals, and white and red lead. Mr. W. H. H. Wetherill, a descendant of the fourth generation, fixes the date of domestic production and the actual establishment of the industry by Wetherill & Sons at 1804. History relates that the factory was burned shortly after it began operation by an Englishman who sailed for London the day following the fire. The factory was rebuilt in 1808 or 1809, despite the threats of English white lead agents that they would crush the enterprise, and which history relates they endeavored to accomplish until the war of 1812 forced them to retire from the American markets and assured the prosperity of the enterprise. Wetherill & Sons undoubtedly used the Dutch process, and utilized horse dung as the source of heat and carbon dioxide. Pulsifer records that they took out several patents and made numerous improvements in both the white and red lead industries.

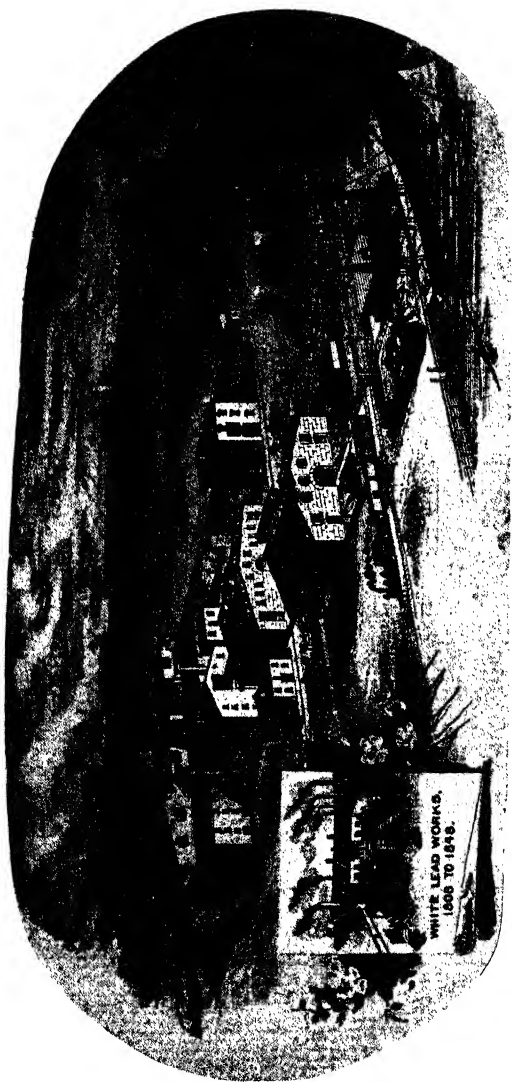


FIG. 2.—WETHERILL WHITE LEAD WORKS.

24. Coxe in an official report to the Secretary of the Treasury in 1810 states that there was only one lead factory in operation at that date and that 369 tons were produced in that year. This report undoubtedly refers to the Wetherill plant.

25. **Effect of the War of 1812.** The war of 1812 made the white lead industry a very profitable one, and it is only natural that the industry developed rapidly. The second plant was built in Philadelphia about 1812 by an Englishman by the name of Smith, who was succeeded in 1813 by one Joseph Richards, who in 1819-20 disposed of the controlling interest to M. Lewis & Co. John Harrison, a chemical manufacturer, also of Philadelphia, began the corroding of white lead by the Dutch process almost immediately after the rebuilding of his chemical works which were destroyed by fire in 1806. The actual date of operation, however, is unknown.

26. **Other Early Manufacturers.** The manufacture of white lead was begun in Pittsburg not far from 1810-12 by Bielin & Stevenson, and at about the same time by Trevor, Pettigrew & Provost, who, however, did not remain in business long. In 1815 a factory was established in Cincinnati by the Cincinnati Manufacturing Company. Bishop in his "History of American Manufactures" states that a corroding plant was established in New York in 1820, but does not state the name of the company. The Brooklyn White Lead Works was incorporated not far from 1825. This firm first endeavored to manufacture white lead by a quick process said to have been devised by a Dr. Vanderberg of Albany, who was the originator of the company. The process, like many later ones, proved unsuccessful and was abandoned for the old Dutch process about 1830, horse manure being used as the fermenting material. In 1832 Mr. Augustus Graham, an active part-

ner of the company, went to England and there secured employment as an ordinary workman in one of the best equipped corroding plants and learned their process and methods in detail and which were introduced in his own plant on his return to this country, the most important improvement being the substitution of tan-bark for horse manure.

27. Adoption of Uniform Scale of Prices. The establishment of numerous other white lead plants and the opening up of new lead ore fields caused a big decline in the price of both metal and white lead, and Pulsifer relates that "In 1830 the manufacturers of the Eastern cities of the United States found it necessary, owing to very strong competition, and probably overproduction, to enter into an agreement for the purpose of maintaining uniform and profitable prices. By the terms of this agreement each factory (there were eight at that time east of the Alleghanies) had the privilege of appointing an agent in eleven principal markets in the Eastern States, from Portland to New Orleans. These agents were to receive a commission of five per cent. The prices and terms fixed by this agreement were as follows:

Dry white lead	8 cents per pound
Pure lead, ground in oil	9 cents per pound
Potters' red lead	6 cents per pound
Glassmakers' red lead	7½ cents per pound

"The terms were:

For quantities amounting to

Less than \$300, 6 months.

From \$300 to \$500, 6 months and 1 per cent discount.

From \$500 to \$800, 6 months and 2 per cent discount.

From \$800 and upwards, 6 months and 3 per cent discount.

“It was stipulated that these amounts were to be purchased at one time to entitle the buyer to these terms.

28. “The parties to this agreement bound themselves in the sum of two thousand dollars, to be considered and treated as stipulated damages, for the full and faithful performance of the agreement, and ninety days’ notice was required to be given of an intention to withdraw.

“The signers of this agreement were Lewis & Company, Wetherill & Sons, Harrison Brothers, of Philadelphia; Hinton & Moore, of New York, who were possibly selling agents for the Union Company, the Brooklyn White Lead Company, of Brooklyn, New York; and Francis Peabody, and the Salem Lead Manufacturing Company of Salem, Massachusetts.”

The production of white lead at this date had reached about three thousand tons and in 1840 to about five thousand tons.

29. **Formation of New Companies.** Between 1840 and 1850 the white lead industry increased rapidly. The following companies were established at about this period:

Eckstein White Lead Company, Cincinnati,	1837.
Atlantic White Lead Company, of New York,	1842.
Jewett Lead Works, of New York,	1844.
Ulster White Lead Company, Saugerties, N. Y.,
Fahnestock White Lead Works, Pittsburgh,	1844.
Eagle White Lead Works, Cincinnati,
The Collier White Lead and Oil Works, St. Louis,	1851.

It is probable that the annual production of white lead in 1850 was about nine thousand tons. Between 1850 and 1860 there was little development in the industry as far as the building of new plants was concerned. The practice of adulterating white lead had grown to such an extent that but little room was left for substantial increase

in the manufacture of white lead, notwithstanding the increase in population and wealth of the country, and the production by 1860 was only about fifteen thousand tons.

30. Effect of the Civil War. The enormous demand for metallic lead at the beginning of the Civil War checked the growth of the white lead industry for a time, although the differential between pig lead and white lead reached almost ten cents in 1864. This enormous profit stimulated the erection of several new plants toward the close of the war, and the period immediately following was marked by a great development of the industry. Among the more important plants erected during this period are:

S. B. Cornell & Son, Buffalo,	1861.
St. Louis Lead and Oil Company, St. Louis,	1865.
Southern White Lead Company, St. Louis,	1866.
D. B. Shipman White Lead Works, Chicago,	1865.
Western White Lead Company, Chicago,
Davis Chambers Lead Company, Pittsburgh,	1866.
Beymer, Bauman & Co., Pittsburgh,	1867.
J. H. Morley White Lead Works, Cleveland,	1867.
Bradley White Lead Works, Brooklyn,
Salem Lead Works, Salem, Mass.,	1868.

31. Patents Issued. Pulsifer states that not less than forty patents were issued during this decade (1860-1890) for improvements in the manufacture of white lead, most of them modifications of the Dutch process or precipitation processes. None of them, however, as far as can be learned proved to be of any economic value. The production of white lead in 1870 has been estimated at 35,000 tons.

32. Between 1870 and 1880 the industry continued to show a healthy development, but was along the lines of expansion and increase of facilities in the plants already



FIG. 3. — LEAD BUCKLE.

established rather than in the building of new plants. Thirty-five patents were issued for improvements in the manufacture of white lead during this decade, fifteen of which were for new processes the majority of which were tried out on a commercial scale but like the preceding inventions were unsuccessful and were abandoned after entailing more or less loss upon the promoters. Since that date there have been comparatively few attempts to develop new processes on a commercial scale, although two at least have proven highly successful and are being carried out on a large scale, viz., the Carter process and the Mild process, formerly known as the Rowley process, both of which, together with the Matheson process and the Bailey process, will be discussed at length in subsequent chapters.

33. Improvements. Since the substitution of tan-bark for stable litter in 1832 by Graham there have been very few improvements made in the methods or details of the Dutch process, and these few relate chiefly to improvements in the washing, screening, and drying of the white lead rather than in the principles or details of corrosion. One or two companies are attempting to separate the corruptions from the metallic cores by a dry process without washing the lead at all and the residual acetates remaining in the white lead are given a treatment with ozonized air to convert them into a less active form. One of the newest attempted innovations is the use of glass corroding pots.

CHAPTER III.

DEVELOPMENT OF THE WHITE LEAD INDUSTRY IN THE UNITED STATES (Continued).

34. Formation of National Lead Trust. In 1887 there was formed an organization known as the National Lead Trust, capitalized at \$90,000,000, which according to the agreement and by-laws was organized for the purpose of securing intelligent coöperation in the business of smelting, refining, corroding, manufacturing, vending, and dealing in lead and all its products and carrying on all other business incident thereto. The corporations forming the trust were:

The Bradley White Lead Company.

Anchor White Lead Company.

The St. Louis Smelting and Refining Company.

The St. Louis Lead and Oil Company.

Brooklyn White Lead Company.

Jewett White Lead Works.

The J. H. Morley Lead Company.

35. Absorption of Other Companies. Within three years from the time the National Lead Trust was formed there had been drawn into and absorbed by the trust according to the evidence in the case of the National Lead Company *v.* S. E. Grote Paint Store Company, Supreme Court of Missouri, 1898, in addition to those enumerated above:

The National Lead and Oil Company of New York.

Ulster Lead Company.

Union Lead Company.

S. G. Cornell Lead Company.
Atlantic White Lead Company.
Davis Chambers Lead Company.
National Lead and Oil Company of Pennsylvania.
Armstrong-McKelvey Lead Company.
Fahnestock White Lead Company.
John T. Lewis & Brothers.
Eckstein White Lead Company.
Kentucky Lead Company.
Maryland White Lead Company.
McBirney-Johnson Company.
Salem Lead Company.
Collier White Lead and Oil Company.
Missouri Lead and Oil Company.
Red Seal Castor Oil Company.
Southern White Lead Company of Missouri.
W. H. Gregg White Lead Company.

36. Dissolution of National Lead Trust. In 1891 the National Lead Trust was dissolved. President Thompson testified that the reasons which led to the dissolution and termination of the trust were:

“Mainly¹ because there had been laws passed by the United States and a number of States that were inimical to that form of organization and a great public prejudice had been aroused which seriously affected the value of the shares of a trust. . . . Besides the capitalization of the National Lead Trust was excessive.”

37. Formation of National Lead Company. In December of that year (1891) the National Lead Company was organized with a capital of \$30,000,000. President Thompson's report to the stockholders of the National Lead

¹ Statement, briefs, and opinion of the Court, *National Lead Company v. S. E. Grote Paint Store Company*, St. Louis Court of Appeals, p. 3.

Company, February 16, 1893, states that "This company was organized for the purpose of taking over all the assets of the National Lead Trust."

38. According to the testimony in the case above cited (redirect examination of President Thompson, page 30) the certificate holders of the National Lead Trust surrendered their trust certificates in the National Lead Trust and received in exchange therefor stock in the National Lead Company, the certificate holders receiving one share of common stock and one share of preferred stock in the National Lead Company for every six certificates in the National Lead Trust and thirty cents cash.

39. **Different Branches of the National Lead Company.** The report also shows that the National Lead Company had the following branches:¹

Atlantic Branch, New York City, proprietors of —

Atlantic White Lead and Linseed Oil Works.

Jewett White Lead Works.

Brooklyn White Lead Works.

Bradley White Lead Works.

Union White Lead Works.

Lenox Smelting Works.

Ulster Lead Works.

Boston Branch, Boston, Mass., proprietors of —

Salem Lead Works.

Buffalo Branch, Buffalo, N. Y., proprietors of —

Cornell Lead Works.

Baltimore Branch, Baltimore, Md., proprietors of —

Maryland White Lead Works.

Cleveland Branch, Cleveland, Ohio, proprietors of —

J. H. Morley Lead Works.

¹ Statements, briefs, and opinion of the Court, *National Lead Company v. S. E. Grote Paint Store Company*, St. Louis Court of Appeals, p. 5. Also Appellants Abstract of the Record, Appeal from the Circuit Court, pages 83 to 91.

Cincinnati Branch, Cincinnati, Ohio, proprietors of —
 Eckstein White Lead Works.
 Anchor White Lead Works.

Louisville Branch, Louisville, Ky., proprietors of —
 Kentucky Lead and Oil Works.
 American White Lead Works.

Chicago Branch, Chicago, Ill., proprietors of —
 Southern White Lead Works.
 D. B. Shipman White Lead Works.

St. Louis Branch, St. Louis, Mo., proprietors of —
 St. Louis Lead and Oil Works.
 Collier White Lead and Oil Works.
 Southern White Lead Works.
 Red Seal Castor Oil Works.

John T. Lewis & Brothers Company, Philadelphia.

Western White Lead Company, Philadelphia.

National Lead and Oil Company of Pennsylvania, Pitts-
 burg, proprietors of —
 Armstrong-McKelvey Lead and Oil Works.
 The Beymer-Bauman Lead Works.
 Davis Chambers Lead Works.
 Fahnestock White Lead Works.
 Pennsylvania White Lead Works.
 American Oxide Works.

Also St. Louis Smelting and Refining Company, St. Louis,
 Mo., proprietors of —
 St. Louis Smelting and Refining Works, St. Louis, Mo.
 Harrison Reduction Works, Leadville, Colo.
 Rio Grande Smelting Works, Socorro, New Mexico.
 St. Louis and Zacatecas Ore Company, Jiminez, Mexico.

40. Operation of Factories. This report goes on to state that "White lead factories disadvantageously located, or

unable from any cause to make their goods on an economic basis, have been discontinued, while others have been greatly enlarged, so that the capacity for production of all classes of goods manufactured by the company has been decidedly increased."

41. Independent Companies. While the National Lead Company owned or controlled a large majority of the white lead plants of this country, there were several which maintained an independent existence, the more important of which were the Wetherill plant of Philadelphia; the Carter Company of Omaha and Chicago; Nevin, of Pittsburg; the Eagle Lead Company of Cincinnati, Ohio; the Gebhardt Company, of Dayton, Ohio; and the Pioneer of San Francisco. Several of these however, were of very small capacity.

42. The Bailey Process. In 1901 the Union Lead and Oil Company of New York was organized and a plant of an intended yearly capacity of 15,000 tons was built, which was to manufacture white lead by the Bailey process, and represented an investment, it is said, of not far from one million dollars.

43. The essential features of this process were the extension of the surface exposed to attack by the corroding vapors. "In this process the melted lead was forced by its own gravity through a perforated plate of thin steel, which forced it into threads or hairs about one one-thousandth of an inch in diameter. The lead solidified and cooled almost as soon as it passed the plate, and was piled on long, shallow trays with slat bottoms. Each of these trays as it received its charge was run back automatically into place in a suitably constructed bin or rack. When all the trays in this rack had been charged with the fibrous lead the process of corrosion began. Mingled vapors of acetic acid, moisture, air, and purified carbonic acid gas were blown in through



FIG. 4. — LEAD FIBRES. — BAILEY PROCESS.

suitable openings at the bottom and sides of the rack, and after circulating freely through the mass, finally escaped. The temperature meanwhile was maintained automatically at the degree most favorable to satisfactory corrosion."

Corrosion was completed in about three days. The product was disintegrated, separated from the uncorroded lead, washed and dried in the usual manner.

44. The United Lead Company. Before the plant was operated at full capacity it was taken over at a much higher figure by an organization known as United Lead Company, a corporation organized in June, 1904, which in substance was a subsidiary corporation of the American Smelting and Refining Company, who presumably desired more suitable or at least other outlets for the pig lead obtained in their smelting operations. The United Lead Company also acquired the Gebhardt plant, the recently built plant of the Boston-Chadwick Company, the Selby plant of San Francisco, and the McDougall White Lead Company of Buffalo, formerly known as the Kellogg & McDougall Company, which operated under what was substantially the Carter process.

45. The Bailey plant apparently proved a colossal failure, as it was shortly afterwards abandoned. This left the United Lead Company with an outlet for only about one-half of the tonnage capacity anticipated, and did not render them the formidable rival of the National Lead Company that was anticipated.

46. Growth of United Lead Company. Further means were taken by the United Lead Company by securing some of the highest talent in the white lead industry with a view of constructing enormous Dutch process corroding plants in different sections of the country, as there were no more independent plants that could be acquired at anything like reasonable figures, the Sterling and Davis white lead com-

panies having been purchased by the National Lead Company. A site was secured at Perth Amboy, N. J., and the construction of the largest white lead plant in the world was begun. This plant was to have a producing capacity of 20,000 tons yearly, and it was rumored that as soon as completed it was to be followed by the erection of an equally large plant in East St. Louis, for which the site had already been secured, and subsequently by another plant in Chicago. This policy if carried out would have resulted in an overproduction of white lead, as the National Lead Company was not then operating all of its plants, and this naturally would have led to a bitter competitive warfare for the supremacy of the white lead markets.

47. Acquisition of the United Lead Company. Apparently the National Lead Company did not care to enter

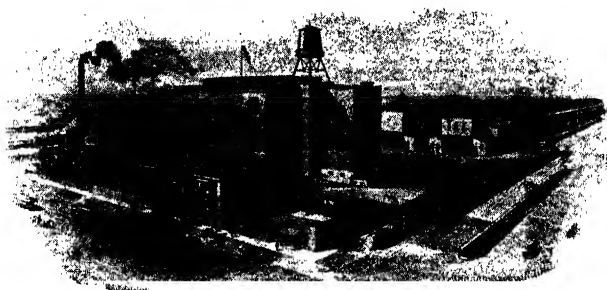


FIG. 5. — WHITE LEAD WORKS. — HAMMAR BROTHERS.

into the struggle, as even before the Perth Amboy plant was entirely completed they acquired control of all of the properties of the United Lead Company, the sale taking place March 8, 1906. This substantially gave the National Lead Company control of approximately eighty per cent of the white lead manufactured in this country, and it has

been strongly intimated that the National Lead Company shortly afterwards obtained a large or controlling interest in the Carter Company,¹ the independent concerns being represented by the Matheson Lead Company, Wetherill & Sons, Harrison Brothers, the Eagle White Lead Company, which had developed a capacity of over twelve thousand tons, the Hammer White Lead Company of about five thousand tons, the Pioneer, and the Rowley, now known as the Mild Process Company, which has recently built a new five thousand ton plant. These companies represented at that time an aggregate capacity of about thirty thousand tons of white lead and oxides.

48. The following is a list of the white lead plants in the United States with their locations and estimated capacities. Those not in operation, as near as the writer can learn, are indicated by leaving the capacity blank. The completion of the Perth Amboy plant in 1907 has doubtless resulted in the closing down of some of the more antiquated plants and probably in reducing the production of several others, as the total estimated tonnage capacity is considerably in excess of the amount of white lead produced. These figures cannot be regarded as exact and can be only considered estimates, as definite information along these lines is very difficult to secure.

¹ See Mineral Industry, 1906, page 520.

NUMBER AND LOCATION OF LEAD PLANTS IN THE UNITED STATES.

Company.	Location.	Process.	Capacity in Tons. (estimated)
National Lead Company.			
1. Atlantic White Lead and Linseed Oil Works.....	New York...	Dutch	12,000
2. Bradley White Lead Works.....	do	do	3,500
3. Brooklyn White Lead Works.....	do	do	4,000
4. Jewett White Lead Works.....	do	do	3,000
5. Ulster Lead Works.....	do	do	2,000
6. Union Lead and Oil Company (Bailey).....	do	Bailey	
7. Union White Lead Works.....	do	Dutch	
8. Boston-Chadwick Company.....	Boston	do	4,000
9. Salem Lead Works.....	Salem, Mass.	do	
10. Cornell Lead Works.....	Buffalo	do	
11. McDougall Lead Company.....	do	Carter	3,000
12. J. T. Lewis & Brothers Company.....	Philadelphia	Dutch	5,000
13. Armstrong & McKelvey Lead and Oil Works.....	Pittsburg	do	3,000
14. Beymer Bauman Lead Works.....	do	do	3,000
15. Davis-Chambers Lead Works.....	do	do	
16. Fahnstock White Lead Works.....	do	do	4,000
17. Sterling Lead Works.....	do	do	4,000
18. Davis Lead Works.....	do	do	3,500
19. J. H. Morley Lead Works.....	Cleveland	do	
20. Eckstein White Lead Works.....	Cincinnati	do	4,000
21. Anchor White Lead Works.....	do	do	4,000
22. Gebhardt White Lead Works.....	Dayton, O.	do	2,000
23. Kentucky Lead and Oil Works.....	Louisville	do	
24. Southern White Lead Works.....	Chicago	do	4,500

Company.	Location.	Process.	Capacity in Tons.
National Lead Company. — (Continued)			
25. D. B. Shipman White Lead Works.....	Chicago.....	Dutch.....	5,000
26. Collier White Lead and Oil Works.....	St. Louis.....	do.....	5,000
27. Southern White Lead Works.....	do.....	do.....	5,000
28. St. Louis Lead and Oil Works.....	do.....	do.....	5,000
29. Selby White Lead Works.....	Valley Junction, Cal.....	Modified Dutch.....	3,000
30. Missouri Lead Company.....	do.....
Carter White Lead Company.¹			
31. Omaha Plant.....	Omaha, Neb.....	Carter.....	7,000
32. Chicago Plant.....	Chicago.....	do.....	14,000
Independent Lead Plants.			
33. Matheson Lead Company.....	New York.....	Matheson.....	2,500
34. Graves Lead Company.....	Camden, N.J.....	Dutch.....	1,500
35. Wetherill & Sons.....	Philadelphia.....	do.....	1,000
36. Harrison Brothers & Company.....	do.....	Carter.....	2,000
37. Nevin Lead Company.....	Pittsburg.....	Dutch.....	1,000
38. Eagle White Lead Company.....	Cincinnati.....	do.....	12,000
39. Hammer Brothers.....	St. Louis.....	do.....	5,000
40. Pioneer Lead Works.....	San Francisco.....	do.....	4,500
41. Lewis Lead Works.....	do.....	do.....	500
42. Mild Process Lead Company.....	Detroit, Mich.....	Mild(Row- ley).....	5,000

¹ Believed by many to be controlled by National Lead Company.

NOTE : As this book goes to press, the writer is informed that a new corroding plant is being built in Newark, N.J., which will be operated by the Eagle Lead Company. Also that the Matheson Lead Company are increasing their capacity largely.

CHAPTER IV.

BRANDS, PRODUCTION, AND PRICES OF WHITE LEAD.

49. Brands. The following are facsimiles (pages 36 and 37), of the chief brands of white lead offered for sale by the National Lead Company, which are now being somewhat unified by the use of the accompanying "Dutch Boy" label. Many of these brands have a national reputation, others have attained their greatest reputation in certain localities because of supposedly distinct qualities and properties possessed by them. In other words, each brand originally had a distinctive and individual significance to the master painter using it. Now, however, as these brands are controlled by a single corporation, there is in the opinion of many no satisfactory assurance that they are any longer made in the same plants as originally. In fact the writer understands that certain brands of white lead each bearing the name of the original manufacturing company and its location are still being offered for sale when as a matter of fact the plants of these former companies have been either abandoned or dismantled. The author does not, however, wish to be understood as stating that the lead offered under these brands possesses less merit than formerly.

50. Short-weight Packages. The adulteration of white lead was exceedingly widespread and attained its greatest prevalence prior to the Civil War. The establishment of several large plants shortly after the close of the war gave a decided impetus to the production and sale of strictly pure white lead. This movement has been steadily growing ever since, and at the present time the writer does not know of a company whose business is strictly the manu-

facture of white lead that offers for sale any white lead but what is strictly free from adulteration. It has, however, been practically a universal custom for many years to offer white lead for sale in short-weight packages, that is, a 50-pound keg of lead weighing 50 pounds gross weight instead of 50 pounds net. In a number of actual determinations made by the writer in 1906 the following shortage in weights was observed:

Number.	Assumed weight.		Net weight.		Shortage.	
	Lbs.		Lbs.	Oz.	Lbs.	Oz.
I	50		46	3	4	0
II	12½		11	13	0	11
III	12½		10	6	2	2
IV	12½		10	7	2	1
V	25		21	12	3	4
VI	25		22	7	2	9
VII	12½		10	0	2	8
VIII	12½		11	0	1	8

Since the passage of laws in several states regulating the sale of paints and paint products, which require net weights and measures to be stated on the label, all or nearly all of the corrodors are offering their leads in full-weight packages.

51. Annual Production of White Lead. Annual production of white lead in the United States,¹ 1884 to 1907.

Year.	Quantity.	Value.	Year.	Quantity.	Value.
	Short tons.	Dollars.		Short tons.	Dollars.
1884	65,000	6,500,000	1896	88,608	8,371,588
1885	60,000	6,300,000	1897	95,658	9,676,815
1886	60,000	7,200,000	1898	96,048	9,400,622
1887	70,000	7,560,000	1899	110,197	11,317,957
1888	84,000	10,080,000	1900	98,210	10,657,956
1889	80,000	9,600,000	1901	100,787	11,252,653
1890	77,636	9,382,967	1902	114,658	11,978,174
1891	78,018	10,454,029	1903	113,886	12,837,647
1892	74,485	8,733,620	1904	117,292	13,026,954
1893	72,172	7,695,130	1905	136,676	15,738,649
1894	76,343	6,662,307	1906	132,081	16,929,250
1895	90,513	8,723,632	1907	127,251	16,448,324

¹ Mineral Resources of United States, 1884-1907.

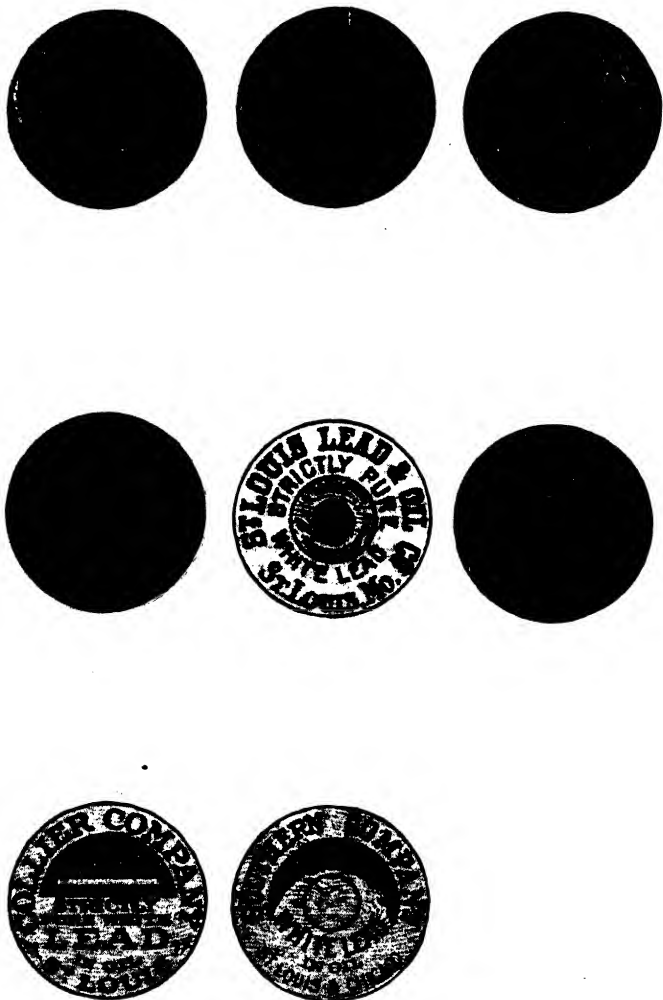


FIG. 6. — FACSIMILES OF LEADING BRANDS OF NATIONAL LEAD COMPANY.



FIG. 7.—FACSIMILES OF LEADING BRANDS OF NATIONAL LEAD COMPANY.

52. Sale of Dry White Lead. White lead is sold by the manufacturers to the wholesale and retail trade ground in about eight per cent of linseed oil or in dry form to the mixed paint manufacturers for use in prepared paints. In order that the reader may gain an idea of the increase in the sale of prepared or mixed paints and its effect upon the sale of white lead in oil the following figures are given, being taken from the United States Geological Records. These figures also serve to show the influence of paint legislation and public agitation along these lines. The effect has not been particularly noticeable in the sale of mixed or prepared paints but rather in the sale of reduced or combination white lead, as at the present date (1908) the writer knows of several large paint manufacturers whose sales of combination white lead have fallen off nearly seventy-five per cent. It is possible, however, that other influences have contributed to produce these results in part.

Year.	White lead in oil.	Dry white lead.
	Tons.	Tons.
1895	76,000	15,000
1903	62,674	51,212
1904	58,332	65,014
1905	62,767	73,909
1906	93,763	38,318
1907	92,216	35,035

53. Differential between Pig Lead and White Lead. The following table showing the variations in price between pig lead and white lead will be of interest.

RANGE OF PRICES PER HUNDRED POUNDS OF PIG LEAD AND WHITE LEAD.¹

Year.	Pig lead.	Dry white lead.	White lead in oil.
1783		9.50	12.50
1784		9.82	11.90
1785		11.90	11.67
1786		9.92	11.43
1787		9.82	11.43
1788		9.82	11.10
1789		10.27	11.10
1790		9.82	10.71
1791		9.82	10.71
1792		9.82	10.96
1793		9.82	11.16
1794		10.71	13.84
1795		11.90	13.39
1796		11.16	12.86
1797		11.30	13.32
1798		11.90	11.68
1799		12.50	14.29
1800		12.50	14.29
1801		14.29	14.29
1802		12.50	13.39
1803		12.50	14.29
1804		13.98	14.88
1805	13.98	13.98	15.00
1806		14.73	16.27
1807		16.74	16.91
1808		16.96	17.32
1809		16.29	17.28
1810		14.29	16.97
1811		14.29	16.97
1812	11.16	17.86	21.43
1813		21.43	24.12
1814		20.54	21.88
1815	17.86	21.43-35.71	21.43-35.71
1816		10.71	14.29
1817		10.71	13.39
1818		10.71	12.50
1819	6.70	11.61	12.50
1820	6.36	11.61	12.50
1821	6.63	10.71	12.50
1822	6.35	10.71	12.50
1823	5.36	10.71	12.50
1824	6.39	10.71	11.61
1825	7.59	10.71	11.61
1826	6.75	10.71	11.61
1827	6.14	10.27	11.61

¹ Mineral Industry, 1894, p. 408. Mineral Resources, 1894-1907.

RANGE OF PRICES. --- *Continued.*

Year.	Pig lead.	Dry white lead.	White lead in oil.
1828	5.39	9.82	11.61
1829	3.75	7.59	9.49
1830	3.75	7.37	8.60
1831	4.56-6.00	8.24-8.73	9.21
1832	5.94	9.50	10.66
1833	5.91	9.50	10.66
1834	5.13	9.35	10.16
1835	6.50	9.86	10.84
1836	6.38	10.00	11.50
1837	5.96	11.12	12.00
1838	5.29	10.75	11.50
1839	5.83	10.25	11.00
1840	4.89	9.75	10.25
1841	4.50	9.00	9.25
1842	3.81	8.00	8.25
1843	3.58	7.75	8.25
1844	3.90	7.25	8.25
1845	4.03	7.50	8.00
1846	4.73	7.00	8.00
1847	4.37	6.90	7.20
1848	4.26	6.18	6.83
1849	4.78	7.31	7.45
1850	4.80	7.00	7.22
1851	4.85	6.75	7.28
1852	4.80	6.31	7.06
1853	6.45	8.75	9.50
1854	6.57	8.50	9.25
1855	6.87	8.75	9.02
1856	6.59	8.37	9.09
1857	6.18	8.25	9.00
1858	5.94	8.50	8.77
1859	5.50	7.25	8.00
1860	5.65	7.25	8.00
1861	5.25	7.27	8.07
1862	6.10	8.20	8.47
1863	6.25	10.44	12.17
1864	7.10	16.72	16.81
1865	6.60	15.58	15.88
1866	6.90	13.41	16.13
1867	6.50	12.73	14.34
1868	6.50	12.19	13.60
1869	6.45	13.27	12.00
1870	6.25	9.64	10.85
1871	6.10	9.68	11.30
1872	6.35	9.41	11.33
1873	9.30	10.62	11.83
1874	6.00	10.50	11.25
1875	5.95	10.00	10.84
1876	6.05	10.00	10.50

RANGE OF PRICES.—*Continued.*

Year.	Pig lead.	Dry white lead.	White lead in oil.
1877	5.45	9.30	9.81
1878	3.60	7.50	8.08
1879	4.18	7.00	7.46
1880	5.06	8.00	8.54
1881	4.89	6.58	7.03
1882	4.91	6.17	6.67
1883	4.32	6.18	6.68
1884	3.74	5.50	6.00
1885	3.95	4.98	5.48
1886	4.63	4.88	5.38
1887	4.50	5.87	6.37
1888	4.42	5.16	5.66
1889	3.93	4.89	5.39
1890	4.48	5.43	5.93
1891	4.35	5.80	6.30
1892	4.05	6.50	6.75
1893	3.69	5.75	6.38
1894	3.29	4.50	5.26
1895	3.23	4.25	5.00
1896	3.03	4.38	4.90
1897	3.64	4.63	5.00
1898	3.79	4.50	5.08
1899	4.53	5.00	5.35
1900	4.55	5.07	5.57
1901	4.21	5.39	5.87
1902	4.21	5.09	5.62
1903	4.23	5.25	6.12
1904	4.42	5.13	6.12
1905	5.28	6.25	6.50
1906	5.83	6.32	6.86

CHAPTER V.

THE MODERN APPLICATION OF THE DUTCH PROCESS IN THE UNITED STATES.

54. Present Importance of the Dutch Process. By far the larger proportion of white lead manufactured to-day is still made by the old Dutch process, so called, and while some of the newer processes have been very successful in their operation, producing high grades of white lead at a cost not exceeding that of old Dutch process white lead, and one or two of them at a very much less figure, yet by reason of the fact that it has meant the introduction of new brands on the market, competing against well-known brands of long standing, the development and expansion of these newer processes has been slow, but at the same time more or less sure, and it is more than probable that within a very few years they will constitute as important factors in the white lead industry as the Solvay and electrolytic processes have in the soda industry.

55. Processes in Use. Confining our discussion at the present time to the white lead industry of the United States and neglecting the large number of experimental and patented processes that for one reason or another have not proven successful in actual commercial practice, the following may be considered as the processes by which white lead is made in this country at the present time:

1. Old Dutch process.
2. Carter process.
3. Matheson process.
4. The Mild process (Rowley).

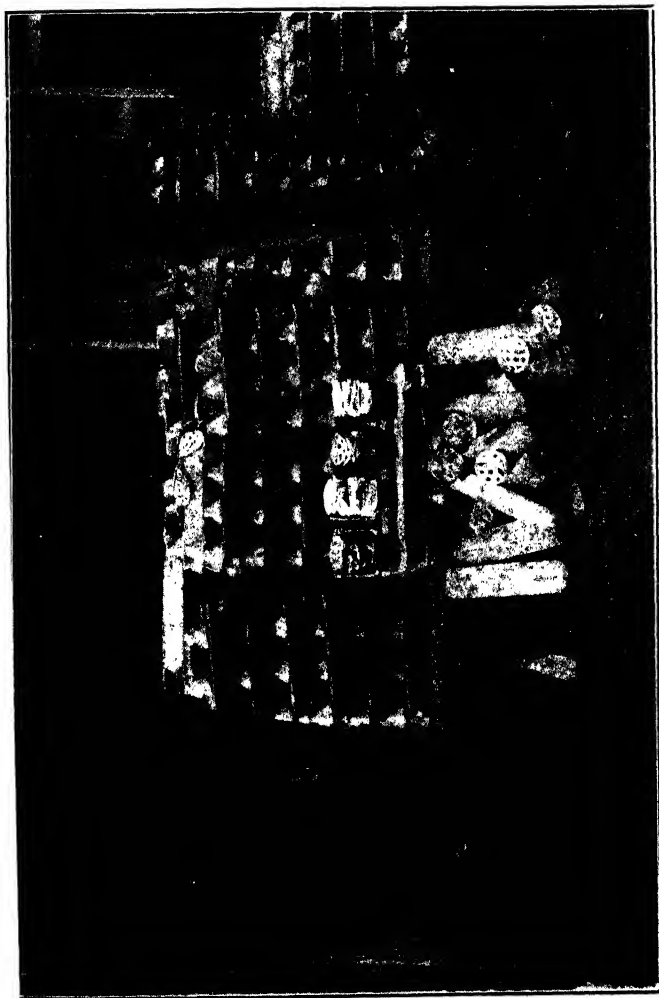


FIG. 8. — FIG I F 'D AND SECTIONS OF CORRODING POTS CONTAINING NEW AND CORRODED BUCKLES.

Several electrolytic processes have been devised, but the writer is not aware that they have yet been developed on a successful commercial scale.

As conducted in this country at the present time the old Dutch process is substantially as follows:

56. Grade of Pig Lead Required. The pig lead used must be a double refined lead, which usually commands a price at least ten cents above the best grades of ordinary refined lead. The following analysis is typical of a good grade of corroding lead:

<i>Constituents.</i>	<i>Per cent.</i>
Silver.....	0.0006
Arsenic.....	0.0050
Antimony.....	trace
Tin.....	0.0003
Copper.....	none
Bismuth.....	0.0100
Iron.....	0.0015
Zinc.....	trace
Manganese.....	none
Nickel and cobalt.....	none
Impurities.....	0.0174
Lead by difference.....	99.9826
	100.0000

The commercial impurity which is the cause of the greatest trouble is bismuth, a lead becoming "common" when it contains as much as 0.0800 per cent of bismuth.

57. Casting the Buckles. The pig lead is melted in a large iron kettle and allowed to flow continuously on to an endless double belt of molds, which form the lead into perforated disks of about one pound each, these disks being commonly known as buckles, due to the fanciful resemblance to the large metallic buckles used as ornaments on

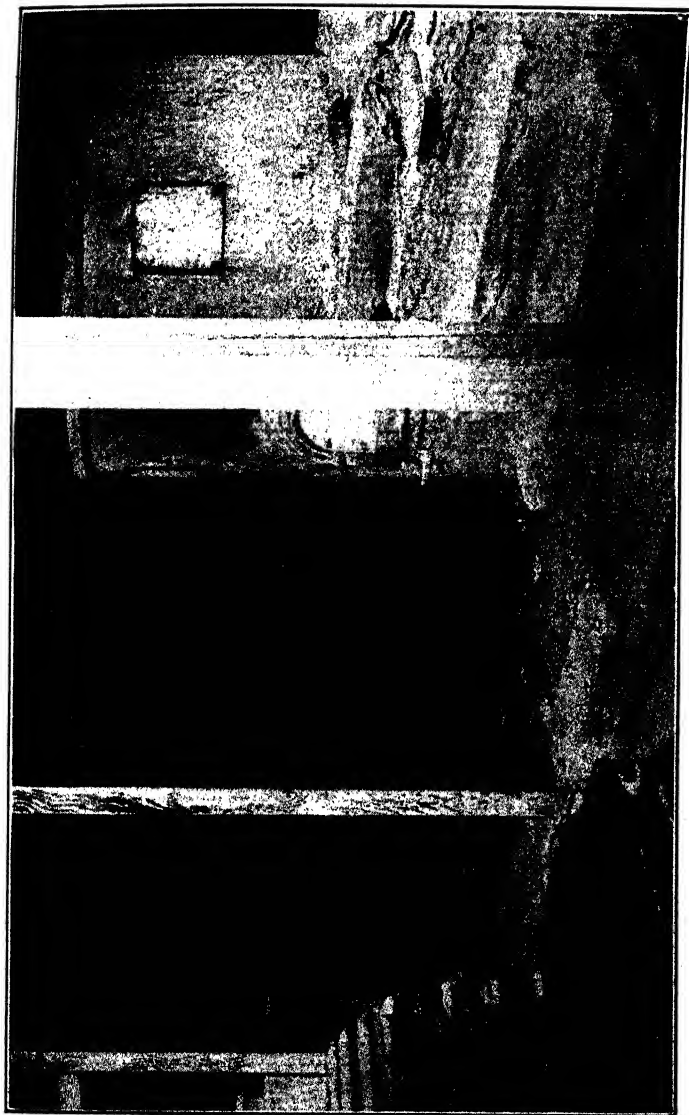


FIG. 9. — BUCKLE CASTING MACHINE.

shoes in the earlier times. It is absolutely necessary that these buckles be cast, as a rolling process would harden or change the crystalline nature of the lead to such an extent that it would be impossible to corrode it. It is therefore extremely necessary that all the parts of the casting system must work in entire harmony — the temperature of the molten lead, the speed with which the chain of molds travels, and length of the mold belt — in order to secure the best results. A double line of molds will cast about eighty buckles per minute. The heat of the molds and the temperature at which the lead is run upon them has a very decided influence upon the ease of corrosion. The buckles are conveyed, generally by wheelbarrows, to the corroding houses, which are compartments square or nearly so, twenty or twenty-five feet each way, located in a large building or shed usually one story in height.

58. Building the Stack. Usually sixteen to eighteen buckles are placed in each corroding pot, about one pint of commercial, number eight acetic acid, diluted to three per cent of true acetic acid, having been placed in the well of the pot. The pots are strongly built of earthenware, the only glazed portion being the well. The loaded pots are then placed side by side on a layer of tan-bark and horse manure about two and one-half feet in depth, and an outer layer about one foot in breadth between the walls of the stack and the pots. About one-third fresh tan-bark is used each time, the other two-thirds being that used in the previous corrosion, sixty to seventy bushels of manure being used to about seven hundred bushels of tan-bark. The tan-bark used is that obtained from tanneries, and in the most modern Dutch process plants it is conveyed from the yard to the stack by means of electric cranes or carriers. The layer of pots is then covered over with a double layer of boards on which is placed more tan-bark, the upper layers

usually being about one foot in depth. More pots are placed on the tan-bark, and in this manner the "stack" so called is built up layer after layer, and when finished is usually ten or twelve layers high, and contains from sixty to one hundred and twenty tons of lead, one hundred tons probably being a fair average. This operation requires the services of four men for about three days. Each layer of pots is connected by a flue or vent leading to the roof, and

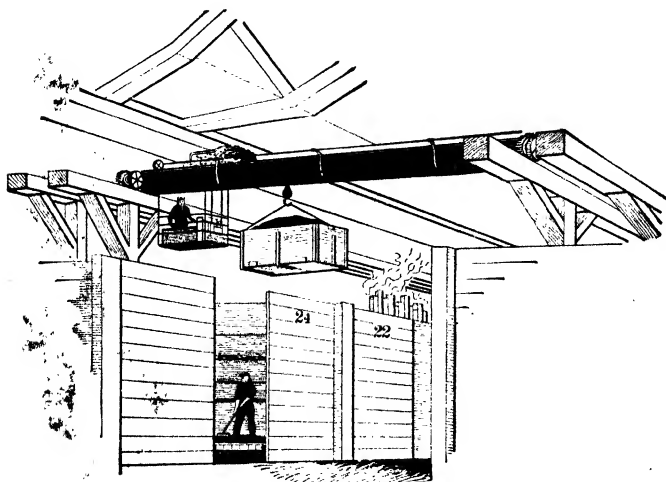


FIG. 10. — ELECTRIC CRANE FOR CONVEYING TAN-BARK. — HAMMAR BROS.

which permits the gases due to the decomposition of the moistened mixture of tan-bark and manure to escape. The temperature and smell of the escaping gases and steam and their apparent volume furnish the only means of judging the conditions inside of the stack and progress of the corrosion, and also the only possible means of regulating these conditions by closing or partially closing the flues, thus controlling to some extent the reactions inside the stack. The temperature if too low will check the corro-



FIG. 11.—FILLING THE CORRODING POTS. — NATIONAL LEAD COMPANY.

sion or retard it entirely; if too high will cause the formation of a crystalline or sandy white lead or even a yellow product which is largely oxide.

59. Reactions Involved in the Corrosion. The stacks are allowed to remain undisturbed for one hundred to one hundred and twenty days. The tan-bark and manure, having been carefully tempered prior to their introduction into the stack, rapidly ferment, the temperature rising rapidly to 160 to 175° F., a temperature sufficient to vaporize the acetic acid and the moisture in the tan-bark. The mixed vapors attack the metallic lead, forming first a basic lead acetate. A large amount of carbon dioxide is also liberated during the fermentation, which reacts with the basic acetate, forming a basic lead carbonate, or what is commonly known as white lead. The transformation of the lead may be represented by the following equations:

1. $\text{Pb} + 2 \text{C}_2\text{H}_4\text{O}_2 = \text{H}_2 + \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2.$
2. $3 \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 2 \text{H}_2\text{O} = 2 \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2$
 $\quad\quad\quad + 2 \text{C}_2\text{H}_4\text{O}_2.$
3. $2 \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2 + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$
 $\quad\quad\quad = 2 \text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2 + 4 \text{C}_2\text{H}_4\text{O}_2.$

Several authorities consider the liberation of hydrogen as improbable and believe the reactions proceed as follows:

1. $\text{Pb} + \text{H}_2\text{O} + \text{O} = \text{Pb}(\text{OH})_2.$
2. $\text{Pb}(\text{OH})_2 + 2 \text{C}_2\text{H}_4\text{O}_2 = \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 2 \text{H}_2\text{O}.$
3. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 2 \text{Pb}(\text{OH})_2 = \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{Pb}(\text{OH})_2.$
4. $3 [\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{Pb}(\text{OH})_2] + 4 \text{CO}_2 = 3 \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
 $\quad\quad\quad + 2 [\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3] + 4 \text{H}_2\text{O}.$

60. These reactions indicate that the acetic acid or the neutral lead acetate is continually regenerated, attacking more of the metallic lead, and the reaction becoming cyclic until the larger portion of the lead is converted into white



FIG. 12. — A LAYER OF CORRODING POTS IN POSITION. — EAGLE LEAD COMPANY.

lead, the operation becoming slower and slower as the crust or coating of white lead on the metal increases in thickness, usually coming to a standstill when 70 to 80 per cent of the metal has become converted. The horse dung acts as the starter for the tan-bark, causing the fermentation to begin more quickly and proceed more rapidly in the initial stages. If it were not for the discoloration of the white lead, due to the action of hydrogen sulphide and other sulphur compounds, the horse dung would be used in much larger quantities, as its action is very much more rapid and complete than that of the tan-bark.

61. Conditions Required for Successful Corrosion. The

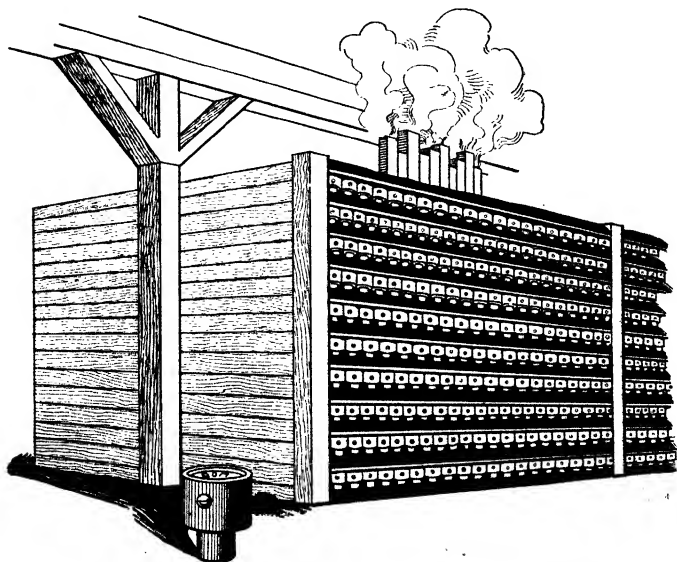


FIG. 13. — COMPLETED STACK. — HAMMAR BROTHERS.

correct tempering of the tan-bark is the most important part of the process. If an excessive amount of water is used, or the water is too hot, or the heap of bark allowed to overheat, the tan will be "killed," as it is termed, i.e.,

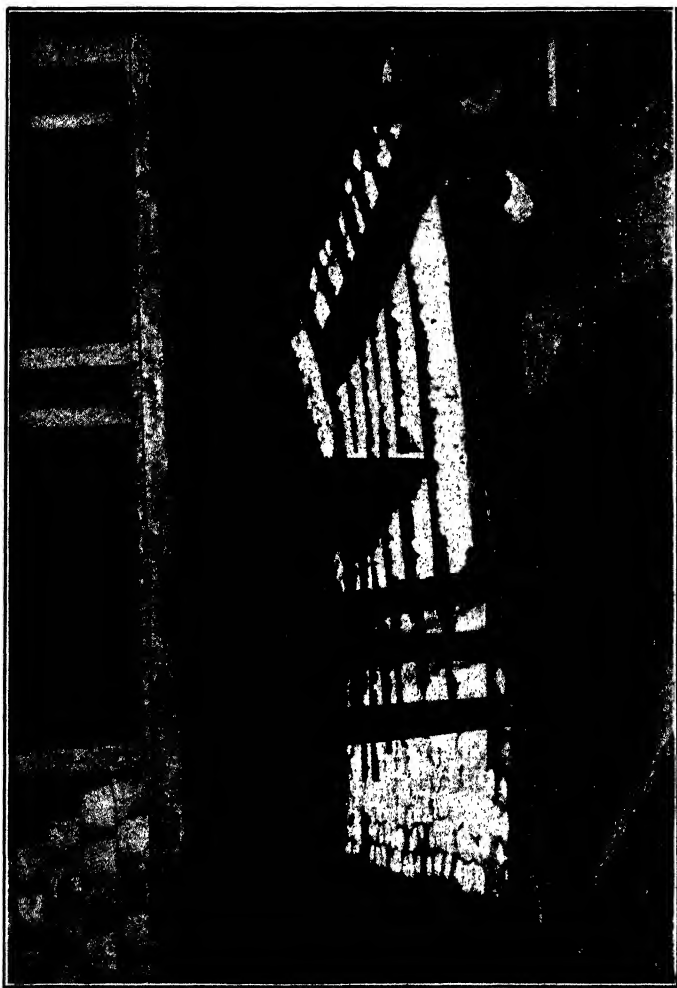


FIG. 14. — A FINISHED CORROSION SHOWING POSITION OF FLUES. — NATIONAL LEAD COMPANY.

the principle which causes the fermentation is checked. Whether this principle is a form of bacteria or an enzyme is not definitely known, but on its proper cultivation depends the success of the corrosion.

62. Taking Down the Stack. At the expiration of the allotted time the stack is taken down in the same manner as erected, except of course the operations are reversed. A considerable number of the pots will be found to be broken, due to the weight of the stack. As long, however, as the well of the pot remains intact it can be used to advantage, because in such instances the corrosion is more nearly complete, as the gases and vapors have freer access to the buckles. The buckles, if the corrosion has been conducted properly, will be found to have become changed into a white hard porcelain-like mass of the same general shape as the original buckle but warped and swollen and usually containing a portion of uncorroded lead in the center. The completeness of the corrosion will vary not only with different stacks but in different portions of the same stack.

63. Very slight amounts of impurities such as bismuth, antimony, arsenic, and zinc will retard the conversion or corrosion very seriously. Great care must also be exercised in the moistening and tempering of the tan-bark. Improper tempering may cause the stack to "die," resulting in a very low percentage of corrosion. Occasionally the fermentation of the tan-bark may be so rapid as to dehydrate the white lead as fast as formed into a yellow oxide. With due care these undesirable results may be avoided, but there are other less troublesome results arising from obscure conditions which cannot be readily controlled, such as soft and fluffy corrosions which require more oil in grinding and have less hiding power.

64. Sandy Lead. If the pig lead or the stack conditions have not been suitable the buckles on being broken will

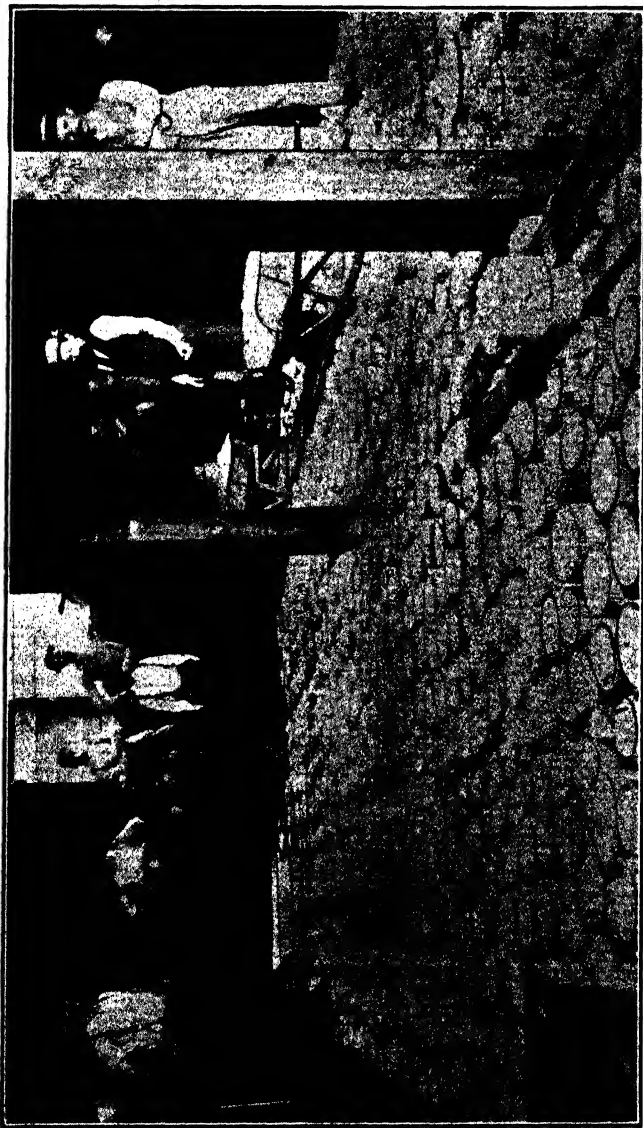


FIG. 15.—TAKING DOWN A STACK. — EAGLE COMPANY.

show a grainy, glistening, crystalline structure due to crystals of neutral lead carbonate. This results in a white lead of diminished hiding power which is very difficult to grind and settles out as a useless sandy lead when thinned down to painting consistency.

Notwithstanding every precaution taken by an experienced corroder, a variable percentage of such lead will be found in every corrosion.

65. The labor item in taking down the stack is very

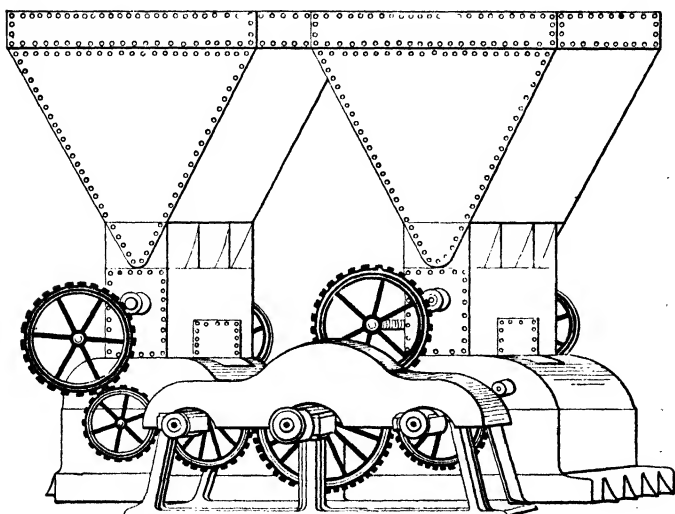


FIG. 16.—CRUSHING ROLLS.

nearly equal to that of putting it up, as the boards have to be taken up carefully in order to avoid getting bits of tan-bark into the pots of corroded lead, and either conveyed to the yard or placed on pegs projecting from the wall. The tan-bark is wheeled or conveyed to the yard; the contents of the pots are also wheeled to the crushing and grinding mill.

CHAPTER VI.

THE MODERN APPLICATION OF THE DUTCH PROCESS IN THE UNITED STATES (Continued).

66. Disintegrating the Buckles. In order to separate the crust of white lead from the metal core the buckles are crushed between large steel grooved rollers and passed through a coarse screen which retains the larger pieces of metallic lead. The portion passing through the screen, which still contains considerable metallic lead, is run through the flattening rolls, which further disintegrate the corroded lead and flatten out the metallic particles so that they are retained on a finely meshed screen. The white lead passing through is ground with water in large stone mills, the grinding surfaces of which have to be frequently recut and dressed, due to the hardness of the white lead particles. In order to remove the metallic lead which often clogs the mills by filling the grooves in the stone, common salt is often put in the hopper in considerable quantities.

67. Washing the Lead. From the grinding mills the white lead is conveyed to the float table or drag box, where the coarser and more crystalline particles are settled out to be reground. The lighter particles are floated off and washed thoroughly in a series of agitator tubs with an increased amount of water to remove as much of the acetic acid and the more or less insoluble basic acetates of lead as possible, the purified white lead finally passing through a fine silk bolting cloth to remove any particles of tan-bark and metallic lead remaining in it.

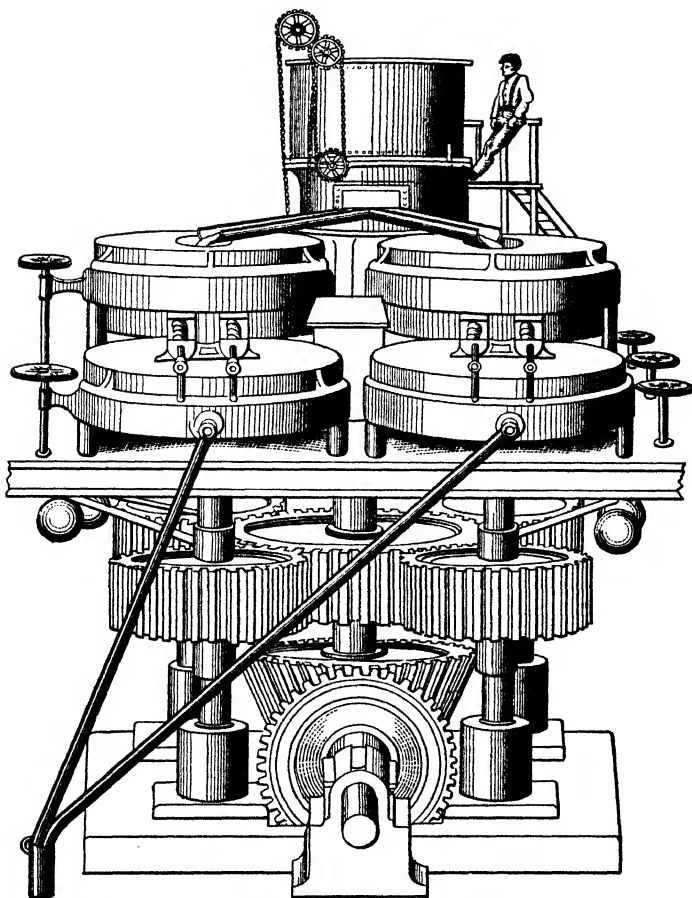


FIG. 17. — WATER GRINDING MILLS. — HAMMAR BROTHERS.

68. Importance of Thorough Washing. The washing of the white lead must needs be thorough, as nearly all the acetic acid used is present in the white lead buckles when removed from the corroding pots, as solid acetate of lead constituting one-half to one per cent of the weight of the buckle and if not properly removed seriously affects the

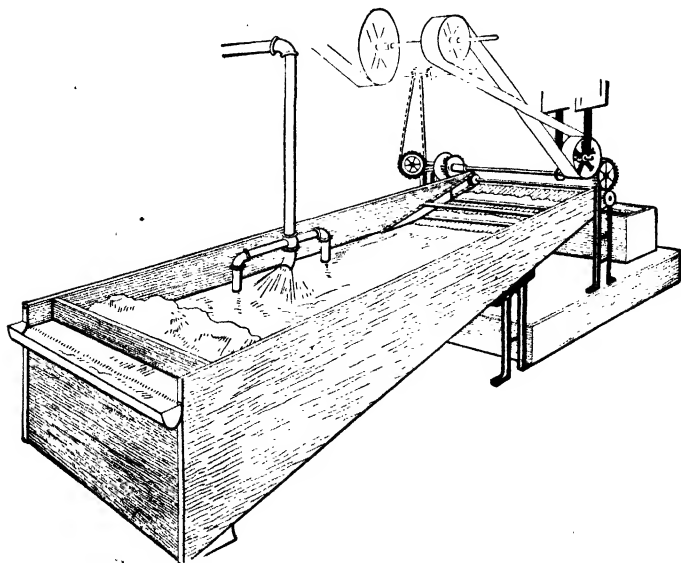


FIG. 18. — DRAG AND WASHING BOX.

service value of the white lead. An eminent paint chemist in discussing this matter says that "slight traces of acetate in the ground lead in oil render it not only far more readily attacked by the blackening influence of the sulphur fumes and sulphuretted hydrogen of the air, but also act upon the linseed oil with which it is mixed, so that it reaches the final state of oxidation and perishes much more quickly than would otherwise be the case, resulting

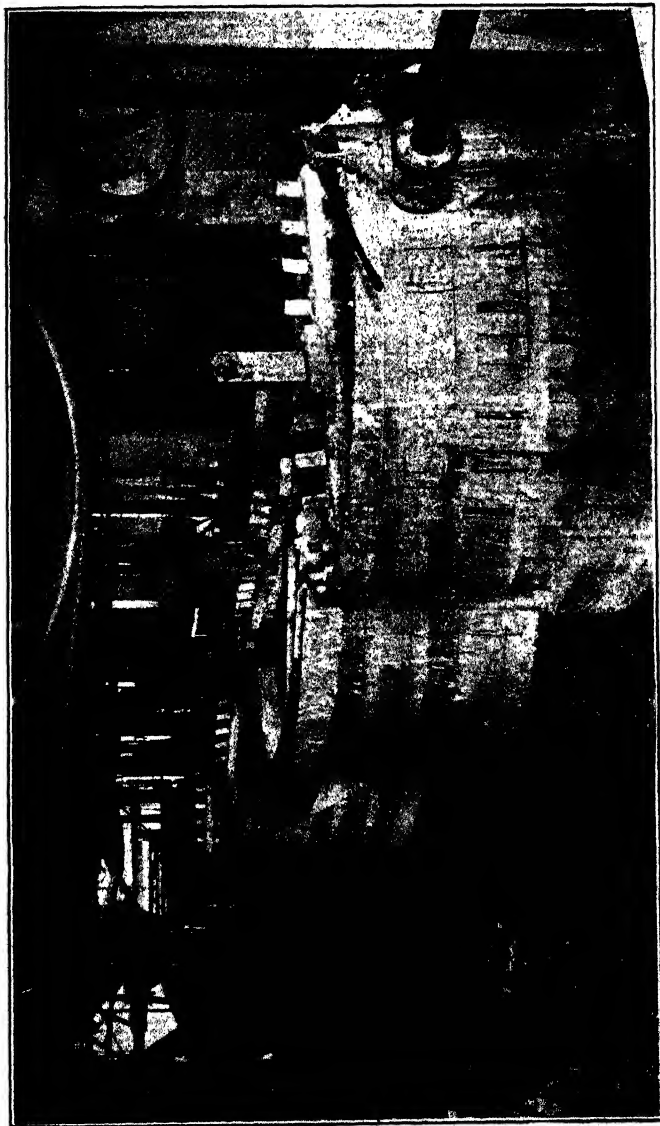


Fig. 19. — AGITATING AND WASHING TUBS. — NATIONAL LEAD COMPANY.

in the rapid chalking of the lead. Under the influence of moisture and the carbonic acid gas of the air complete corrosion and change of the basic carbonate into the transparent crystalline normal carbonate may also take place when acetate of lead is left in the finished product."

69. Drying the Lead. After having been pumped to large settling tanks, where the excess of water is drawn off, the white lead paste, carrying fifty to sixty per cent of water, is pumped on to large copper drying pans usually arranged in series three to four pans high. The dimensions of the pans will vary in the different plants; eight feet in width by about sixty feet in length is a very common size. Each pan is jacketed and so constructed as to withstand considerable pressure, the steam circulating from one pan to the next in the same series.

70. The paste lead is usually pumped on to the pans to a depth of about six inches, and as soon as it has dried to a solid consistency it is marked off into squares, which ultimately causes the formation of cracks as the lead shrinks and thus hastens the drying. About six to eight days are required to dry the pasty mass moisture free. The lead is removed as soon as thoroughly dry, as over-drying tends to the formation of a crust which is hard to grind. It is then taken from the pan with the aid of wooden shovels and packed dry in barrels by means of a mechanical barrel packer or sent to the mills to be ground in oil.

71. Loss of Lead in Washing. The large volume of wash waters used in this process entails a considerable loss of lead, a portion of which is recovered by the more careful corrodors by precipitating out with sodium carbonate; even with this precaution and the use of large settling tanks a considerable amount ultimately finds its way annually into the sewer.

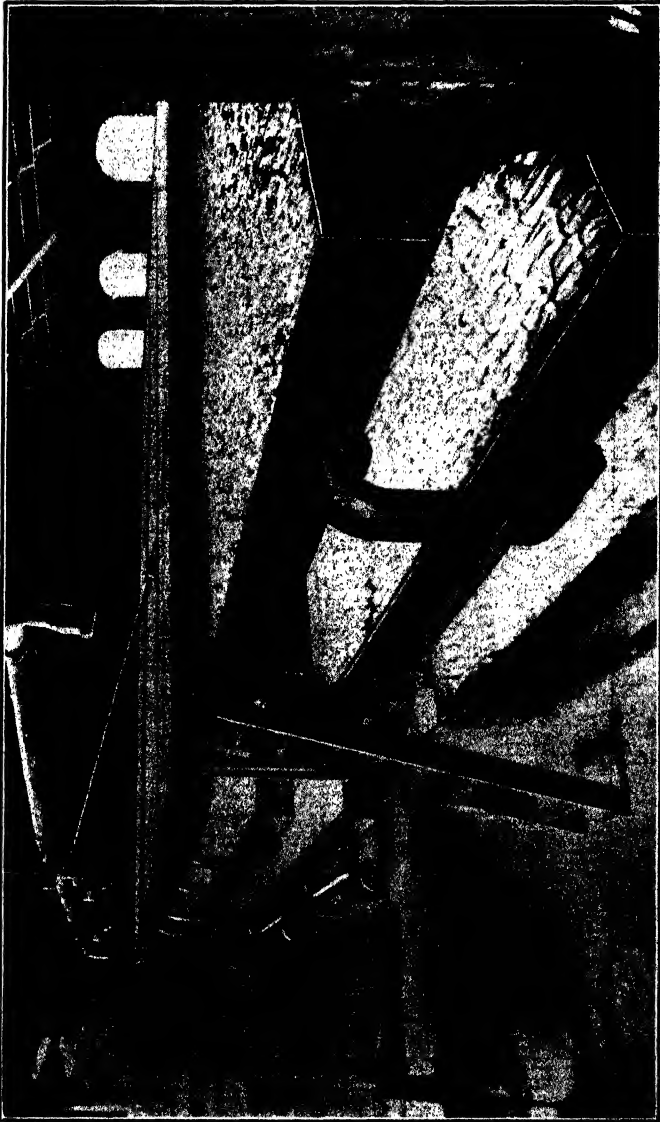


FIG. 20.—DRYING PANS. — EAGLE COMPANY.

72. Effect of Sandy Lead in Paints. The utility of white lead for certain purposes depends quite largely on the care exercised in freeing it from "sandy" lead, i.e., the dense, hard grains of crystalline carbonate due to over-corrosion or unequal distribution of the corroding agencies. In interior brush work or in dipping paints where the white lead is thinned with a considerable amount of turpentine or benzine the sandy lead will rapidly settle out as a useless sediment, and it is the firm belief of the writer that the majority of old Dutch process white lead would be considerably better for the removal of at least three to five per cent of crystalline lead.

73. Cost of a Stack Operation. The following figures as to cost and yields are believed by the writer to be fairly representative, as they are obtained from a run of a one-hundred-ton stack for the usual corroding period, with average conditions and prices. These figures are exclusive of all costs and expenses outside of the stack.

<i>Materials composing stack.</i>	<i>Cost.</i>
210,000 buckles equivalent to 200,000 pounds of lead at \$6 per hundredweight.....	\$12,000.00
10,000 corroding pots.....	600.00
4,000 pounds acetic acid.....	80.00
Lumber (portable).....	130.00
100 cords tan-bark.....	350.00
Labor setting up stack.....	40.00
Labor taking down stack.....	30.00
Miscellaneous.....	20.00
	\$13,250.00

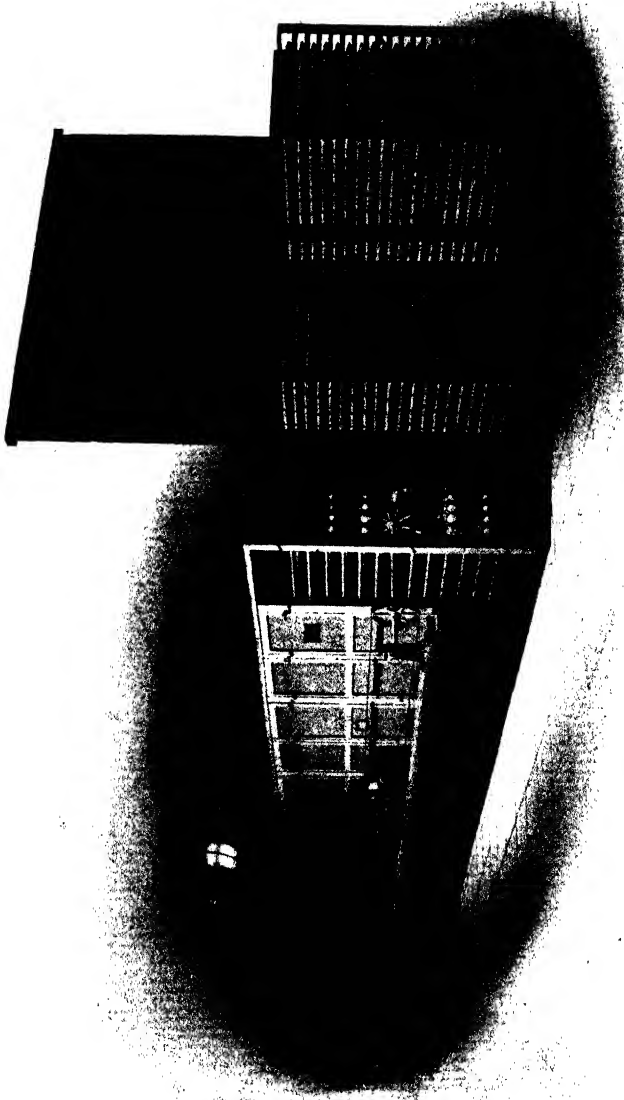


FIG. 21.—IMPROVED WHITE LEAD DRYER. (Courtesy Philadelphia Textile Machinery Company.)

<i>Products obtained.</i>	<i>Value.</i>
178,000 pounds white lead at 6 cents per pound	\$10,680. 00
50,000 pounds uncorroded	3,000. 00
6,000 pounds tailings	210. 00
Lumber fit to reuse	120. 00
Pots less breakage	565. 00
Tan-bark, two-thirds to be used over	233. 00
	<hr/>
	\$14,808. 00

Increase in value \$1,558. 00

Increase in product

200,000 lbs lead set

50,000 lbs. lead uncorroded

150,000 lbs. lead corroded = 178,000 lbs. white lead.
6,000 lbs. tailings.

184,000 lbs. total yield.

184,000 lbs.

150,000 lbs.

34,000 lbs. chemical increase = 22.7 per cent.

Theoretical chemical increase = 24.8 per cent.

74. It should be stated that these figures were obtained during a year in which there was practically no difference between the price of pig lead and dry white lead, this being an exceptional occurrence, as there is generally a marked difference between the two, resulting in a much greater profit, which can be readily calculated by inserting the prevailing market values.

75. **Economy of Process.** While it is probable that labor-saving devices and appliances have not been utilized to the greatest extent possible, in the majority of old Dutch cor-

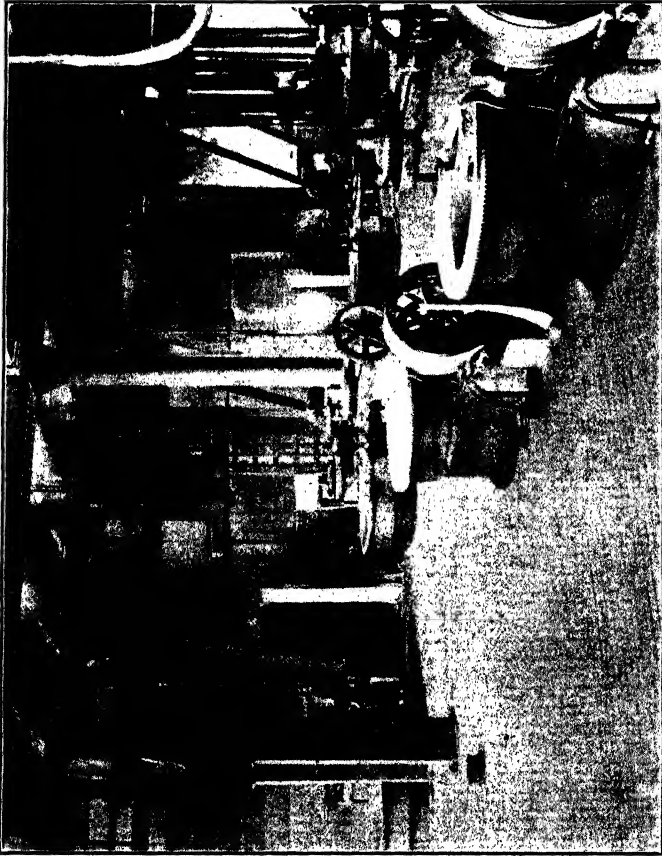


FIG. 22. — WHITE LEAD MIXERS. — EAGLE COMPANY.

roding plants, the nature of the process itself is not conducive to mechanical economies. Nevertheless the art is much more advanced in this country with respect to labor-saving appliances and the preservation of health among the workmen than in Europe. This is especially true with regard to the washing and drying of the white lead.

76. Variation in Quality. There has been considerable controversy during the past few years, especially among the master painters, as to whether the old Dutch process white lead of to-day is the equal of that produced by the same process in less recent years. In this country, as explained in a previous chapter, the large majority of the white lead plants are under the control of a single corporation having a central office which receives the regular routine reports of the various factories as regards labor, materials used, yields and details of process, and it is only natural that each plant would endeavor to obtain the greatest percentage of corrosion with the least expense, and with a process which admittedly does not give a uniform product at all times, it is easy to see how quality may at times be sacrificed for quantity. It was formerly the custom of the most careful corrodors to sort and separate out the imperfect corrosions, and in addition age their lead by storing in large bins for a considerable length of time before grinding in oil, and the writer understands that this custom still prevails among the conservative English manufacturers to-day.

77. Lack of Proper Grinding of White Lead. While the practice discussed above may have a considerable bearing on the question, the present-day practice of grinding white lead by the manufacturers of this country has, in the opinion of the writer, very much more to do with the service or wearing value of white lead than most investigators and writers have been led to believe. The writer

has visited several of the largest white lead plants in the country, and found them grinding their white lead in oil in a double set of stone mills which *were not water-cooled*, with the obvious result that as the day progressed the mills became hotter and hotter, and after five or six hours of steady running the lead as it came from the mills averaged in three specific cases 262° F., 280° F. and 284° F., the temperatures were taken by the writer himself, and were from different mills and represented two different factories. These figures have been repeatedly verified by the writer in numerous plants, and temperatures as high as 300° F. have been noted at the close of the day's run, and yet according to the records of the operator of the mill no temperature higher than 125° F. was recorded. It is not an easy matter to ascertain accurately the temperature of the lead just as it emerges from the mill, and it was much easier for the workman to take the temperature of the lead as it dropped into the keg, some little distance from the mill, and by that time the lead was fairly cool and his figures not far from correct. This practice of grinding hot lead is much more general, the writer believes, than most paint authorities imagine.

78. Changes that may take place in Grinding. Two of the most powerful aids in producing a chemical reaction or combination, where the tendency of the substances to combine is not pronounced, are *heat* and *pressure*, and in a large, uncooled white lead mill running steadily for ten hours, the above-mentioned conditions are certainly attained to a high degree, and a more or less pronounced combination of white lead and linseed oil must inevitably take place with the formation of a lead soap, possibly accompanied by further structural changes in the white lead molecule. This, in the opinion of the writer, is the reason why much of the white lead manufactured in this country chalks

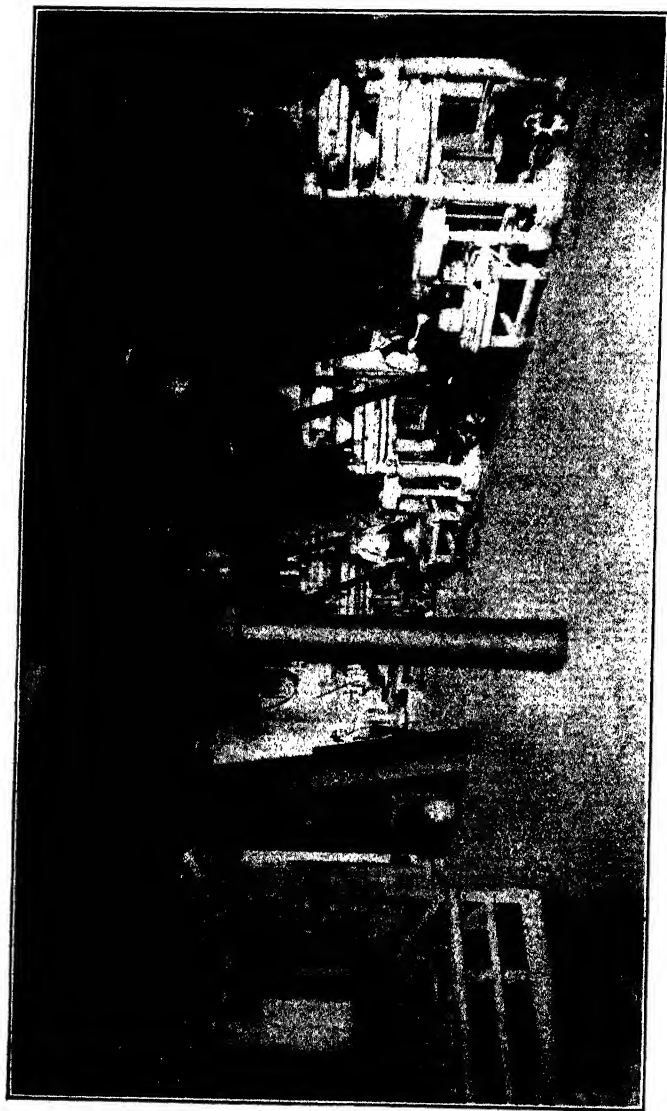


Fig. 23.—OIL GRINDING MILLS.

more readily and does not possess the wearing qualities of the more carefully ground English leads. One of the foremost authorities on the manufacture of white lead, in a letter to the writer, confirms this view with the following statement: "I do not feel that it is safe to heat white lead over 150° F., — preferably not over 125° F., as, if it is heated above the higher temperature, saponification is apt to ensue, with toughening of the mixture, discoloration and actual change in the nature of the material."

79. English Methods of Grinding. The method still followed by the more conservative English manufacturers of using roller mills for incorporating the lead with oil has much to commend it in avoiding these difficulties. A leading English authority, in discussing this subject with the writer, stated that "many of our large English firms have tried the American water-cooled mills, but with very disappointing results. Two London firms, in particular, installed six of these mills, but have thrown them out and are using the English combination roller mills." The writer believes that the cooling effect of the water-cooled mill has been overrated, as the stones are such exceedingly poor conductors of heat that the grinding face of the stone may be exceedingly hot, and yet the other surface which is in contact with the water may be comparatively cool; in other words, the cooling effect of the water is really very slight, unless there is, as often is the case, a tendency for the mill to heat up very hot, 260 to 300° F., in which case the water will exert a considerable cooling effect, but with temperatures around 200° F. and below, the cooling effect is almost negligible, especially during the summer months. The degree of heating will of course depend on how "tight" the mill is set: The writer has repeatedly observed temperatures as high as 255° F. in the most approved types of water-cooled mills, when a "close grind"

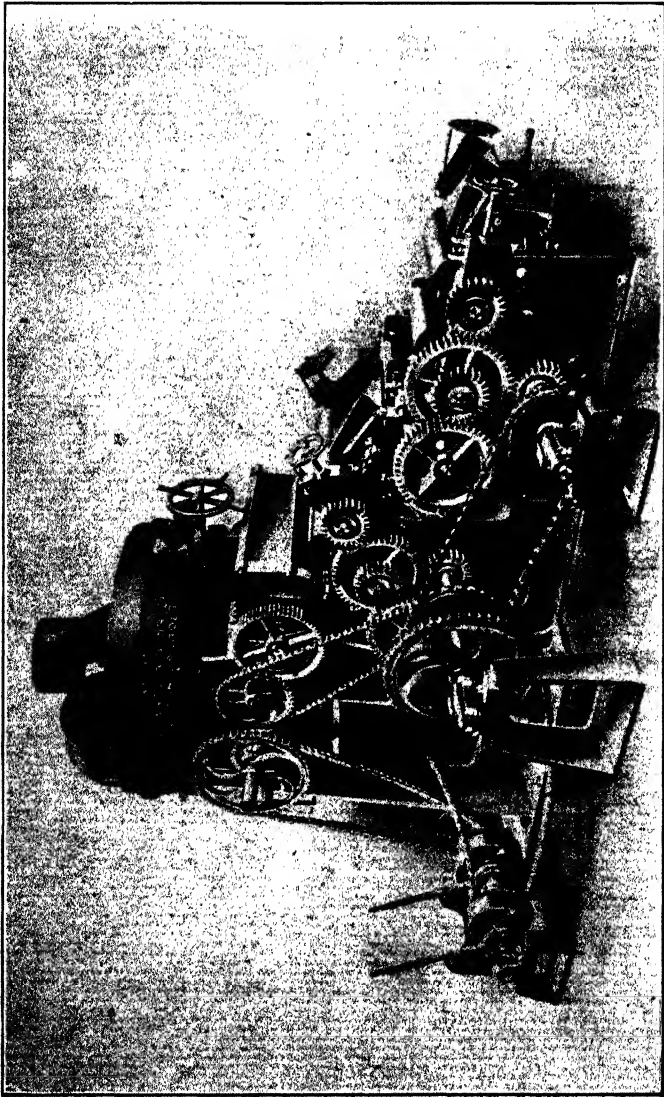


FIG. 24. — ENGLISH TYPE OF WHITE LEAD MILL.

was required, and that, too, as early as two o'clock in the afternoon.

80. Combination Leads. Neither are the manufacturers of combination white leads, so-called, always exempt from the above criticisms, and many of the ills ascribed to the use of combination leads, such as hardening in the keg, are more often due to the practice of grinding in hot mills than to the inert materials employed, although some inert pigments, notably silica, tend materially to aggravate the heating of the mill.

81. The English mills have a much greater capacity than is conceded them by the advocates of the American system of grinding. The type of mill illustrated in this connection, having a 7-foot chasing pan and fitted with 33-inch by 16-inch tandem triple granite rolls is capable of turning out from 8 to 10 tons of white lead per day, while a 40-inch American mill will seldom exceed 3 tons.

82. Pulp Ground Lead. Another means of incorporating white lead with oil has come into use during the last fifteen or twenty years and affords a product which has obtained much favor in the Eastern section of the country. The writer refers now to "pulp" ground lead. In this process the paste of lead and water which would otherwise be pumped onto the dry pan is pumped into a carefully measured and weighed box placed on stationary scales, and the actual weight of white lead present in the paste determined, the correct amount of oil added and the contents of the box dumped into a tall, very narrow upright mixer. Owing to the greater affinity of the oil for the lead a continuous separation of water takes place, which rises to the top, while the stiff paste of lead and oil works to the bottom and is carried off by a screw conveyor either to a grinding mill or is filled directly into the kegs. If the latter, the percentage of water will usually be over

0.5 per cent, while if it has been ground in a mill, sufficient heat is usually generated to bring the water content below 0.5 per cent. Prepared as described above, "pulp" ground lead may contain a considerable amount of acetate of lead.

83. Characteristics of Pulp Lead. The easy working of this lead under the brush and its apparently great whiteness has led to its being received with much favor, especially in the East. However, Hooker, in discussing the value of pulp ground lead, expresses the writer's own views on the subject when he states: "A critical comparison between pulp ground lead and regularly ground lead would not seem to justify this use of pulp lead when durability and permanence of color are concerned." "Pulp lead" is usually distinguished from regular lead by rather a flat, dull look and a little whiter color than the other lead; it will also stand a little more oil in first thinning, but "breaks" suddenly when thinned too far. A small amount rubbed upon a palette or glass with the addition of just a trifle of dry eosine (an aniline dye insoluble in oil) shows at once a bright pink color, due to the production of an eosine lake by the acetate of lead solution present. True, this acetate of lead does not represent to exceed one per cent ordinarily of the lead, but it has a strong bearing upon the saponification of the oil and consequent durability of the paint. A comparison with regularly ground lead shows no such reaction. Now place the two leads, "regular and pulp" ground, upon a glass, and note the effect, when they are rather rapidly dried, as would be the case when the glass is left for a time on the top of a heated radiator. The pulp lead turns rapidly yellow, showing the yellowing effect of the heat on the saponified oil in the pulp lead. The action of gases such as sulphuretted hydrogen present in the atmosphere, particularly of cities,

is very generally known, so far as the blackening of white lead is concerned, but the marked difference between different white leads as regards susceptibility to this influence is not generally known. Placing a little pulp lead in oil upon glass beside regularly ground lead in oil, and subjecting both to the influence of this gas diffused in air, it will be seen that the pulp lead is badly blackened before the action is scarcely appreciable upon the other, showing plainly how much more susceptible to discoloration the pulp ground lead is than the other.

84. The points which have created a certain demand for pulp ground lead are, first, its color, which is fictitiously white, in that it loses this when the water evaporates, besides discoloring more readily than any other; the extra thinners which it will carry and still retain a certain peculiar brushing quality; the seemingly greater covering, which proves false when entirely dry, and the readiness with which it can be used to produce a certain "flat" finish for inside work. The last might be worth some consideration were it not that it is so greatly offset by the sensitiveness of the lead to discoloration, and the rapidity with which it acts upon linseed oil, due, doubtless, to the acetate that was not removed, thus causing the paint to chalk and perish far more rapidly than would a regularly ground lead. Such lead should never be used and be expected to stand any length of time.

CHAPTER VII.

THE CARTER PROCESS.

85. History. Numerous efforts have been made and much money spent in attempting to shorten the time required for the manufacture of white lead by the old Dutch process, but the various quick processes as they were termed did not possess all of the elements of success and after a short trial were given up as impracticable or unprofitable on a large scale. The Carter process, however, was the first in this country to prove the exception to the rule, and at the date of writing, the two plants of the Carter Company in the United States have an aggregate yearly tonnage of approximately twenty thousand tons.

86. Adams White Lead Company. The original patents of what is commonly known as the "Carter Process" were taken out by McCreary & Adams in the early seventies who formed a corporation and operated a small plant in Baltimore, Md., under the name of the Adams White Lead Company. The plant was operated for only a short time. A little later another attempt was made at Washington, Pa., which was likewise unsuccessful, owing to imperfections in the process and crudeness in operation, and also to lack of sufficient capital.

87. Omaha White Lead Company. In 1878, S. E. Locke secured a license from the Adams White Lead Company to operate a plant in Omaha, Nebr., and to this end organized the Omaha White Lead Company which was composed of a number of Omaha capitalists. Besides the manufacture of white lead the company dealt in glass and painters' supplies.

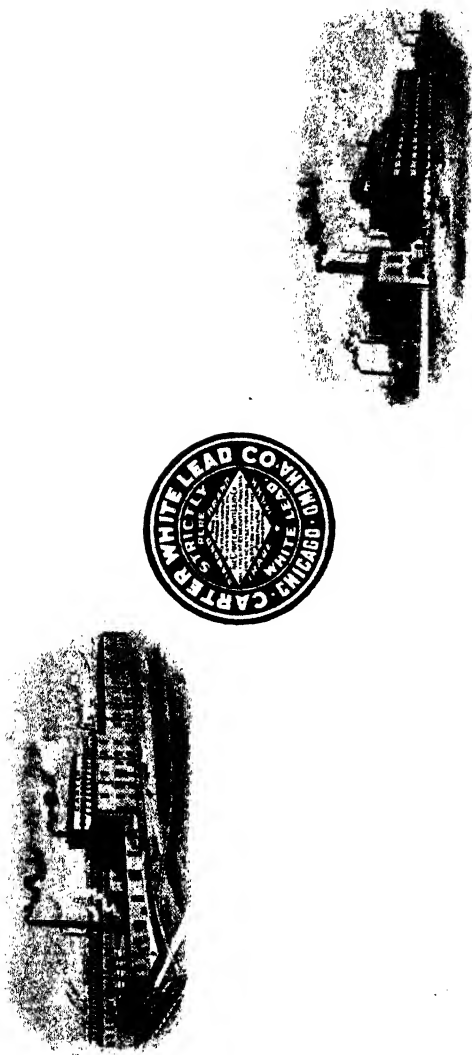


FIG. 25.—PLANTS OF CARTER WHITE LEAD COMPANY.

A banker by the name of H. W. Yates, being one of the largest owners, placed his nephew, S. B. Hayden, in charge of the company. Owing, however, to the lack of experience the company became financially embarrassed.

88. Formation of the Carter Company. Levi Carter, at this time a member of the firm of Coe & Carter of Omaha, large railroad contractors, saw the possibilities of the process and secured in 1885 a controlling interest in the plant which then had a capacity of about four hundred tons yearly. The reorganized company, the name of which had been changed to the Carter White Lead Company, encountered exceedingly bitter competition from the then recently consolidated white lead interests but, due to the indomitable character and perseverance of Mr. Carter, the company managed to keep the plant in operation with a continued improvement of the products produced until it was destroyed by fire in 1890. Profiting by the experience obtained, new capital was secured and a plant of about seven thousand tons yearly capacity was immediately built in East Omaha by Mr. Carter, which began operation in the fall of 1892.

89. The success with the new plant was immediate, the enterprise proving so profitable that the building of a large plant in Chicago was decided upon, and which was completed and put in operation in 1896, having a capacity of about fourteen thousand tons. Later a plant of about five thousand tons capacity was built in Montreal with the aid of Canadian capital.

90. Underlying Principles. The principles underlying this process are the same as in the old Dutch process, but by increasing the area of attack and the use of a more concentrated supply of carbon dioxide, and the continued removal of the crust of white lead from the metal, the corrosion into white lead is accomplished in approximately twelve days,

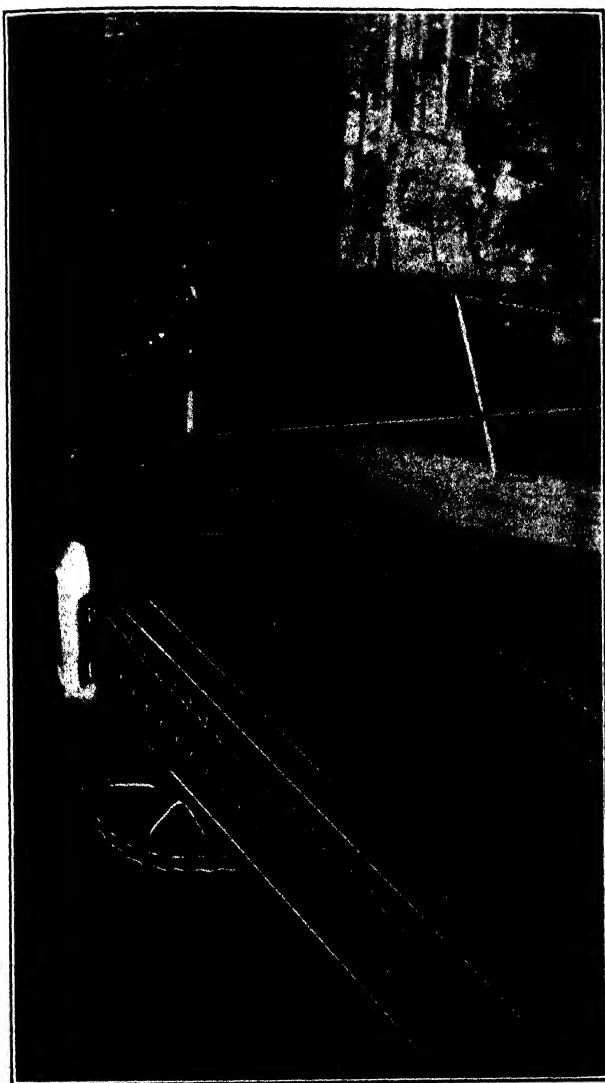


FIG. 26. — LEAD CONVEYER AND MELTING KETTLE. — CARTER PROCESS.

whereas as the old Dutch process requires one hundred to one hundred and twenty, and the percentage of converted lead is eighty-five to ninety per cent as against about seventy-five per cent in the older process.

91. Granulating the Lead. The lead, which is of the same nature and grade as used in the Dutch process, is melted in a large kettle holding about ten thousand pounds, the pigs of lead being conveyed and dumped into the kettle by means of an endless chain. The stream of molten lead as it flows from the kettle encounters a jet of high pressure steam which disintegrates it into a coarse granular powder, which collects in the hopper-shaped bottom of the large blow room and is discharged into truck cars placed underneath. By the use of a slight vacuum any fine particles of lead dust are conveyed to a dust collector, thus avoiding danger to health in the loading of the cars. Charges of about four thousand pounds of this "blown lead" are placed in large wooden drums ten or twelve feet long, and about five or six feet in diameter. Around the tub at each end is a heavy iron hoop resembling a car-rail; these rest on roller bearings; around the center of the tub is another hoop, containing gear-teeth, which in turn mesh into the gears from the large driving shaft which runs the entire length of the corroding room, which contains nearly three hundred of these tubs or drums. The drums revolve slowly, making about six revolutions per hour, which causes the lead to continually shift position, that which is carried up the side of the drum rolling again to the bottom. This exposes each granule to the action of the corroding agencies and also by abrasion wears off the coating of white lead as fast as it forms, continually exposing fresh metal to be acted upon.

92. Corrosion. Dilute acetic acid and water are sprayed into the drums at intervals during the first three days, 30 per cent acetic acid being used, which has been reduced

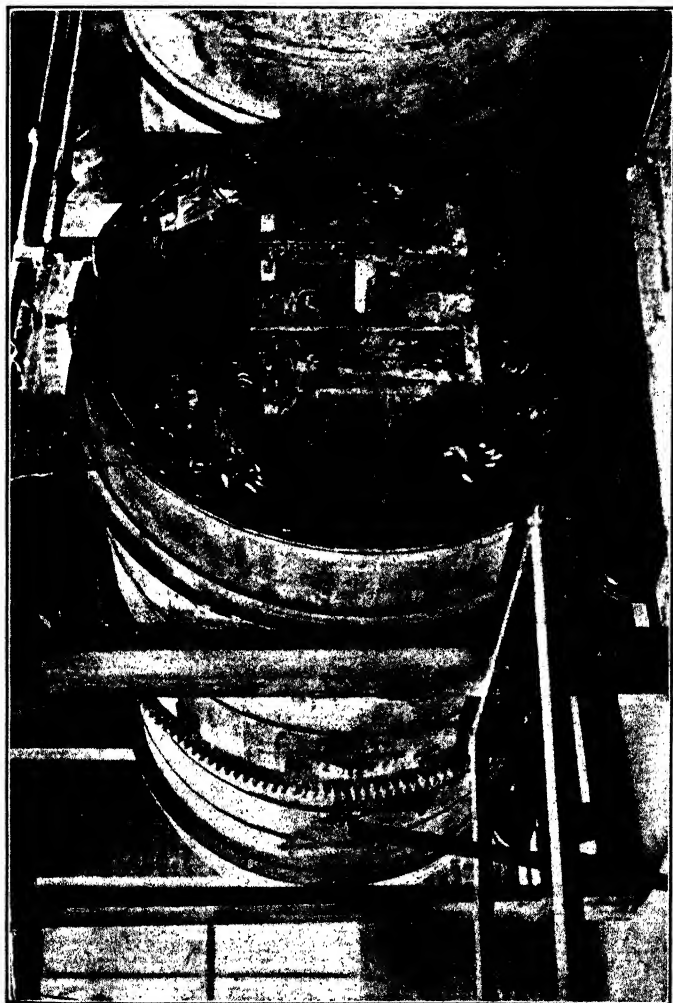


Fig. 27. — CORRODING CYLINDER. — CARTER PROCESS.

one part with four parts of water. The amount used during the corrosion being one and three-quarters to two pounds of 30 per cent acetic acid per hundred pounds of metallic lead, considerably more than used in the Dutch process. A current of purified flue gas containing eight to ten per cent of carbon dioxide is passed through the cylinders, entering through the center of one end and coming out at the other. This gas is obtained by burning a very high grade of coke, low in sulphur, under the boilers, and is purified by passing it through a compartment filled with bog iron ore, which removes all traces of sulphur, and also gives an opportunity for any soot particles to deposit. The temperature of the gas will vary between 150° and 200° F., as it is delivered to the drums. In order to secure an even and uniform corrosion the partially corroded mass is removed from the drums about the sixth day, and run through a pulverizer to reduce any lumps or balls that may have been formed.

93. The disintegrated material is then replaced in the drums and the conversion finished, the entire corroding process taking about twelve days. Great care must be exercised in not adding too large quantities of water or acid, or granulating the lead too fine in the first place, as in such instances the mass becomes so pasty as not to work properly in the drums, or is "drowned out" as the workmen term it, which results in an almost entire cessation of chemical action, and can only be "started" again by mixing with a large amount of fresh lead and recorroding. The chemical actions that take place are entirely similar to those of the old Dutch process and in fact, the Carter process differs not at all in the fundamental principles from the older process.

94. Washing and Floating. The finished product on removal from the drums is run into large tanks, where it is

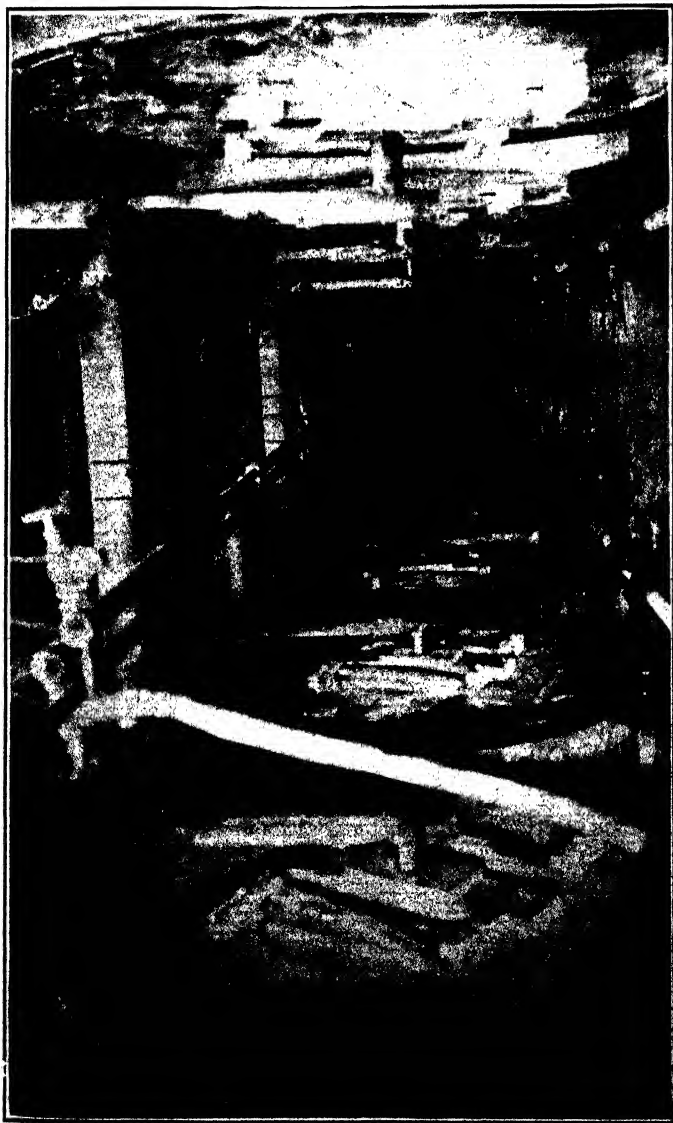


FIG. 28. — CORRODING ROOM. — CARTER PROCESS.

agitated with water and then washed through a rotary screen to remove coarse particles, the finer material is then passed through a drag and float system to remove the last trace of blue lead and as much of the crystalline lead as possible. The separated white lead is washed thoroughly to free it from acetic acid, and the more or less insoluble acetates of lead, which are afterwards precipitated from the wash waters with carbonate of soda. The washed lead is allowed to settle in large tanks, the supernatant water drawn off, and the thick paste pumped onto copper drying pans and dried in the usual manner.

95. Chemical Composition. In chemical composition the ratio of carbonate to hydroxide is fairly constant, the following table showing the composition every two weeks for a period of twelve months.

	Carbonate.	Hydroxide.
May 31, 1906.....	73.59	26.41
June 15, 1906.....	75.23	24.77
June 30, 1906.....	76.26	23.74
July 15, 1906.....	71.89	28.11
July 31, 1906.....	73.23	26.77
Aug. 15, 1906.....	69.65	30.35
Aug. 31, 1906.....	72.86	27.14
Sept. 15, 1906.....	71.16	28.84
Sept. 30, 1906.....	73.84	26.16
Oct. 15, 1906.....	75.11	24.89
Oct. 31, 1906.....	72.50	27.50
Nov. 15, 1906.....	75.29	24.71
Nov. 30, 1906.....	74.68	25.32
Dec. 15, 1906.....	77.41	22.59
Dec. 31, 1906.....	76.81	23.19
Jan. 15, 1907.....	74.44	25.56
Jan. 31, 1907.....	74.93	25.07
Feb. 15, 1907.....	75.77	24.23
Feb. 28, 1907.....	77.11	22.89
Mar. 15, 1907.....	75.65	24.35
Mar. 31, 1907.....	74.62	25.38
Apr. 15, 1907.....	76.32	23.68
Apr. 30, 1907.....	77.72	22.28
Average.....	74.61	25.39

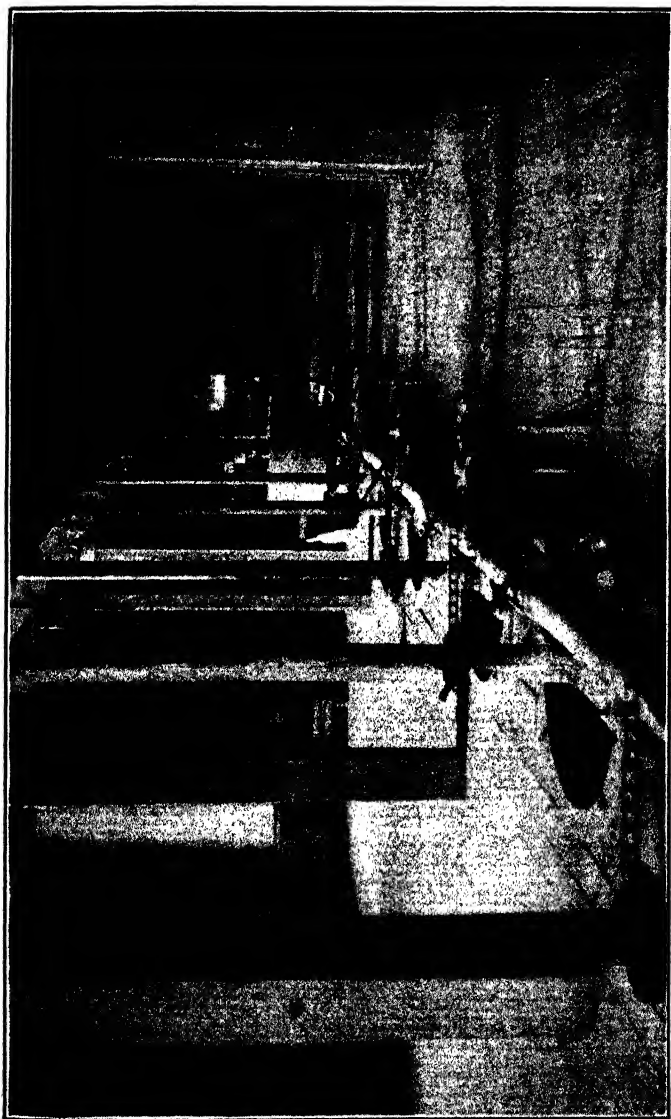


FIG. 29. — CHASER AND MIXERS. — CARTER PROCESS.

It will be noted that the percentage of carbonate is slightly higher than in the average grades of old Dutch white lead, which together with its freedom from blue lead explains its clearness of tone. In the practical paint tests, made by the writer, little or no difference has been observed in its wearing or service value, as compared with the best brands of old Dutch lead; in application it works slightly easier under the brush, and remains in suspension better in the oil.

96. Characteristics. As produced by this process, Carter lead is usually whiter than old Dutch white lead, the particles are much finer and of a more nearly uniform size, and, therefore, 100 pounds of Carter lead in oil will cover a considerable larger area of surface than 100 pounds of old Dutch lead when reduced alike with oil. The body or hiding power, however, is not at all times quite equal to that of the older lead, although the surface is distinctly a cleaner, clearer white.

97. Success. This process having proven very successful financially, a plant was built along similar lines by Harrison Brothers & Company, Philadelphia, in which the Carter Company was interested in a way, and assisted towards the construction of the plant. Shortly afterwards another plant was built at Buffalo, by Kellogg & McDougall, of about three thousand tons capacity, with the assistance of the same engineer who constructed the Harrison plant. Both of these plants have been eminently successful.

CHAPTER VIII.

THE MILD PROCESS (ROWLEY).

98. Derivation of Name. The "Mild Process" for manufacturing white lead is the only one in practical operation in this country which does not require the use of strong acids, alkalies, or other chemicals in the process of manufacture, every trace of which must be removed from the finished product, necessarily involving certain purifying processes which in themselves are expensive and costly and if incomplete will cause a marked deterioration in the quality of the lead produced.

99. This process derives its name from the very fact that it is the mildest, simplest, most natural process possible for the manufacture of white lead — metallic lead, air, water and carbon dioxide gas being the only substances required. This process results in the production of one uniform product, a strictly pure basic carbonate of lead of approved chemical and physical constitution and of a whiteness, density and covering power not exceeded by that of any other make of white lead.

100. Early Attempts. The proposition of reducing granulated lead by attrition in the presence of water and carbonating the product obtained is a comparatively old idea and numerous attempts have been made and several patents have been taken out embodying this idea, not only in England and on the Continent but in this country as well. Pulsifer in his History of Lead records the attempts of Welch and Evans of Philadelphia in 1814 who patented a quick process of making white lead, by which granulated

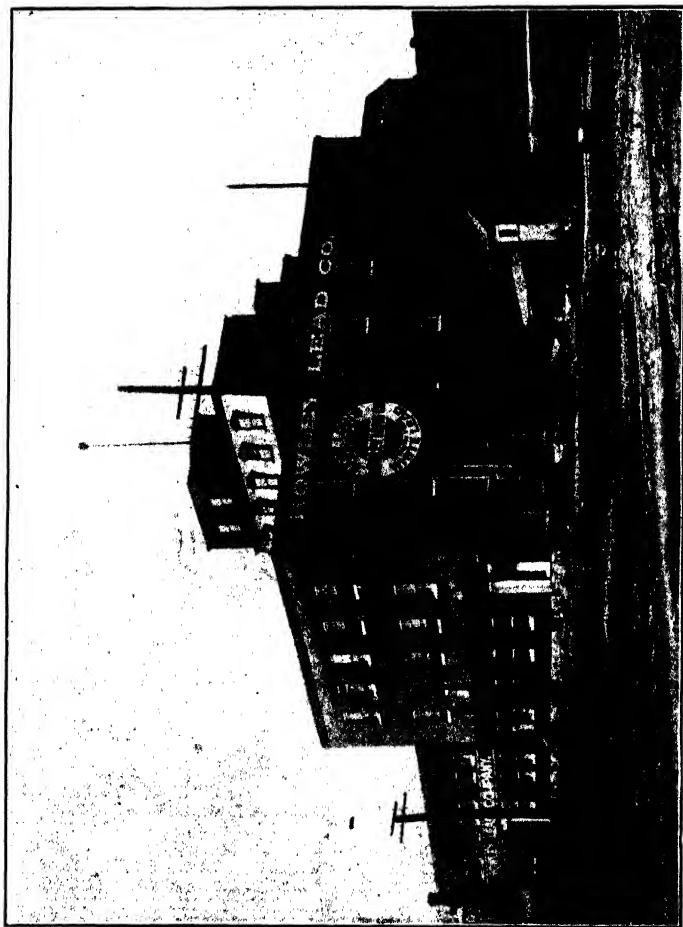


FIG. 30. — PLANT ROWLEY LEAD COMPANY.

lead was placed in lead-lined barrels, which were made to revolve. The barrels were partly filled with water, and the particles of lead removed by attrition were oxidized by oxygen from the air, and this oxide carbonated by the introduction of carbon dioxide produced from burning charcoal. Also that of Smith Gardner, of New York, who took out a patent in 1840, for a process by which "granulated or small pieces of lead were introduced into vessels lined with sheet lead, and partially filled with water, and so arranged that they could be revolved or manipulated in such a manner as to subject the lead to continual attrition. The vessels were kept closed, and during the process carbon dioxide and air were introduced."

101. Solution by W. H. Rowley. Owing to a lack of knowledge of the correct principles by which this process must be conducted in order to be successful all of these earlier attempts failed when put to practical test on a commercial scale and it remained for Mr. Willson H. Rowley of St. Louis, Mo., to overcome the difficulties encountered by his predecessors and put this type of process into successful operation on a large scale.

102. Early Training. Unlike the majority of inventors who have worked along the line of attempting to render the process of white lead manufacture more rapid and economical, Mr. Rowley had the advantage of many years experience in the white lead industry, having been connected with the Carter White Lead Company, besides having had a close acquaintance with the old Dutch Process of manufacture through employment with the Southern White Lead Company with which his father, Mr. G. A. Rowley, was connected for some years.

103. Atomization with Superheated Steam. Mr. Rowley's predecessors had been able to obtain only a coarsely granulated lead to start with, which could be reduced to

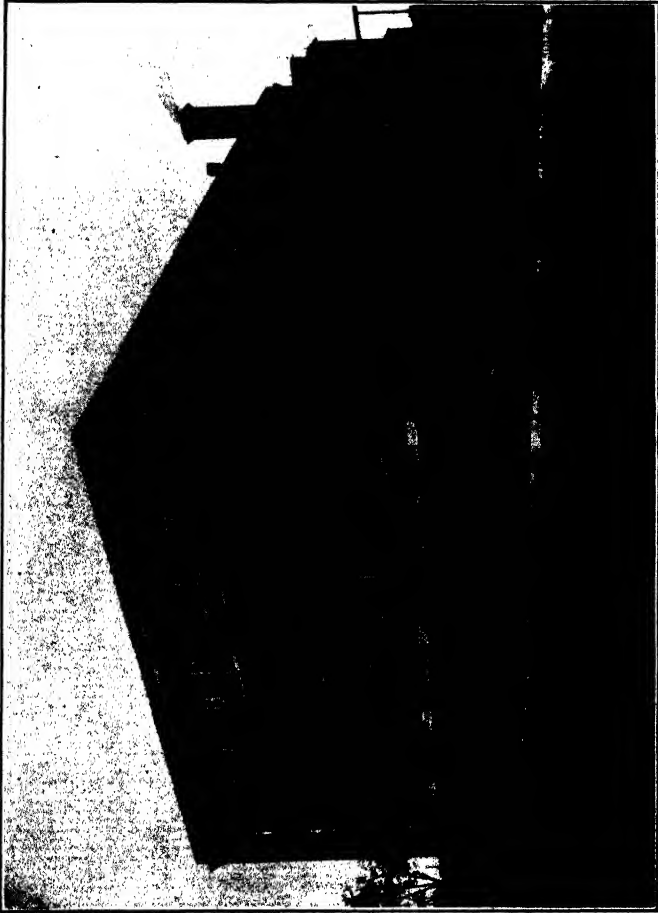


FIG. 31. — MILD PROCESS LEAD PLANT.

oxides or basic hydroxides only with great difficulty by attrition in the presence of water and air. His experiments, however, led him to conceive the idea of atomizing or disintegrating the lead with the aid of a current of high pressure superheated steam. His experiments along this line which were carried out on an extensive scale were completely successful and the several patents covering the processes of manufacture were granted Mr. Rowley in 1902 and 1903.

104. Growth of Process. Immediately thereafter a plant of approximately 1000 tons annual capacity was equipped and placed in operation early in the same year. The product found immediate consumption and by 1907, the sales having outgrown the producing capacity of the plant, it was found necessary to enlarge the factory or build a new one. The latter proposition was the one decided upon as the most feasible and resulted in the building of the present plant in Detroit, additional capital having been interested in the enterprise, and the name changed from the Rowley White Lead Company to the Mild Process White Lead Company, affiliated with the Acme White Lead & Color Works. The present plant is one of the largest and most modern equipped white lead factories in the world, having when fully equipped an annual capacity of over 5000 tons. The mechanical devices installed for reducing the amount of labor to a minimum in the handling and conveying of the lead in the different stages of manufacture render this process the most economical of any in use and at the same time the most sanitary.

105. Simplicity of Process. The process by which this simple and progressive conversion from metallic lead into white lead is accomplished is extremely simple. The coroder is not obliged to use the extremely highly refined

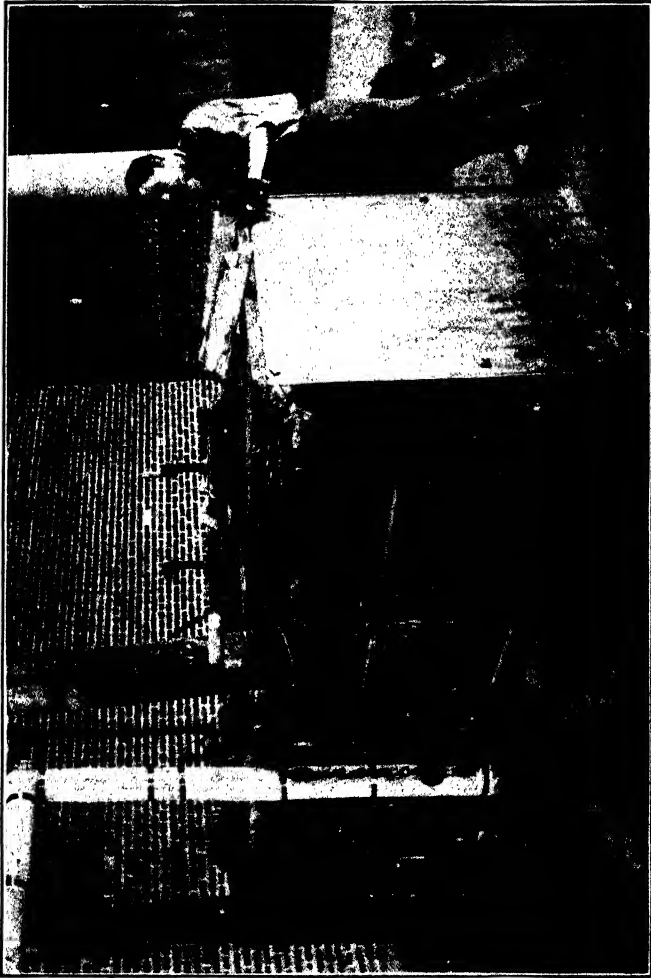


FIG. 32. — ATOMIZING APPARATUS. — MILD PROCESS (ROWLEY).

lead used by the Dutch process, but may use an ordinary good grade of lead; some of the hard grades of lead, however, do not suffer conversion as easily as the softer varieties, although there is apparently little or no difference in the color and quality of the product obtained.

106. Atomizing the Lead. The lead is melted in large kettles holding 5,000 pounds each from the bottom of which it is conveyed through heated pipes to the "atomizers," which are similar in principle to the ordinary laboratory blast lamp. In the atomizers the molten lead comes in contact with a current of steam superheated to a temperature higher than the melting point of the lead. The expansive force of the steam disintegrates the lead into exceedingly minute particles, which immediately solidify. Each of the four atomizers in the present plant has a capacity of 1,500 pounds of atomized lead per hour. The streams of atomized lead are directed downward in a large steel room some two stories in height, in the bottom of which are about two feet of water. By means of a drag-and-screw conveyor the lead, in the form of a very heavy mud, is delivered from the blow-basin to the pump-feeder, which keeps the particles suspended in the water so that the material can be handled by a rotary pump, which forces the lead and water through a pipe line to the float boxes, where the lead is deposited in the desired compartments, the water flowing back to the blow-basin again, which insures against any loss of lead. There are five float boxes in each of the two lines, and when filled each line has a capacity of 250,000 pounds of lead.

107. Oxidizing and Hydrating. By means of gate valves the lead is discharged into the oxidizers directly underneath, six to ten thousand pounds to the oxidizer as desired. The requisite amount of water is added, a current of air under low pressure from a fan introduced and the



FIG. 33. — BLOW BASIN, PUMP FEEDER AND ROTARY PUMP. — MILD PROCESS (ROWLEY)

contents agitated mechanically for twenty-four to thirty-six hours. The particles of lead during the atomizing process have already become coated with a thin pellicle of suboxide which renders the lead very active chemically, so that within a very few hours after the beginning of the agitation a strong chemical action sets in accompanied by a marked rise in temperature, resulting in the formation of any of several basic hydroxides of lead as may be desired, which will vary in color from greenish yellow through the different shades of yellow orange, to a brownish orange, these results being secured by varying the amount of water, air, agitation and control of the temperature. Some of these basic hydroxides are much more suitable for white lead making than others. At the expiration of the twenty-four to thirty-six hours, according to the size of the charge, about eighty to ninety per cent of the lead will have been converted and the oxidizers are discharged into a trough emptying into the float system, where by means of an inclined drag, two agitator tubs and a float-table the metallic lead is separated from the basic oxide and returned to the float boxes, to be added to a fresh charge of atomized lead in the oxidizers.

108. The separated basic hydroxide is conveyed by means of another rotary pump to the fourth floor where it is deposited in a series of large tanks, the water being returned to the separating system again thus avoiding any mechanical loss of lead.

109. Carbonating. The above-mentioned tanks also act as a storage for the basic hydroxide, which is drawn as required into the carbonators located on the floor below. The carbonators are large cylinders somewhat similar to the oxidizers in construction but of less capacity; in them the basic hydroxide of lead is agitated in the presence of flue gas containing about eighteen per cent of carbon



FIG. 34. — FLOAT BOXES, OXIDIZERS AND DISCHARGE TROUGHS. — MILD PROCESS (ROWLEY).

dioxide. By means of scrubbers the flue gases are thoroughly cooled, desulfurized and freed from soot particles. For the first twenty-four hours no apparent change is noticed in the color but in the next twelve hours the change is very rapid and is accompanied by a remarkable swelling or increase in volume of the mass, the carbonators requiring to be watered at short intervals, both on account of the swelling of the mass and the combining of the water with the lead. In approximately thirty-six hours the carbonation is complete, resulting, if the operation has been properly conducted, in an exceedingly white basic carbonate of lead of very closely the theoretical composition. As there are no impurities present, no washing or floating is necessary, and on withdrawal from the carbonators the white lead is pumped directly onto the dry pans and dried in the usual manner; when dry it crumbles instantly under the slightest pressure into a very fine powder and therefore does not have to be run through a disintegrating mill before it is barreled dry.

110. Control. The "Mild Process" is under a much more complete control than any of the other processes, as any slight variations that may take place in the chemical actions involved can be easily corrected and counter-balanced. At first thought it might seem that a white lead produced in this manner would consist largely of a mixture of hydroxide and normal carbonate, but such is not the case as may be demonstrated both by a microscopical examination and by a close study of the process of formation of the white lead. The composition of the basic hydroxide formed indicates a hydration of ten to twelve per cent, or about one-third of the amount to be found in the finished white lead. Therefore the larger part of the hydroxide portion of the molecule is formed during the carbonating process and this has much to do

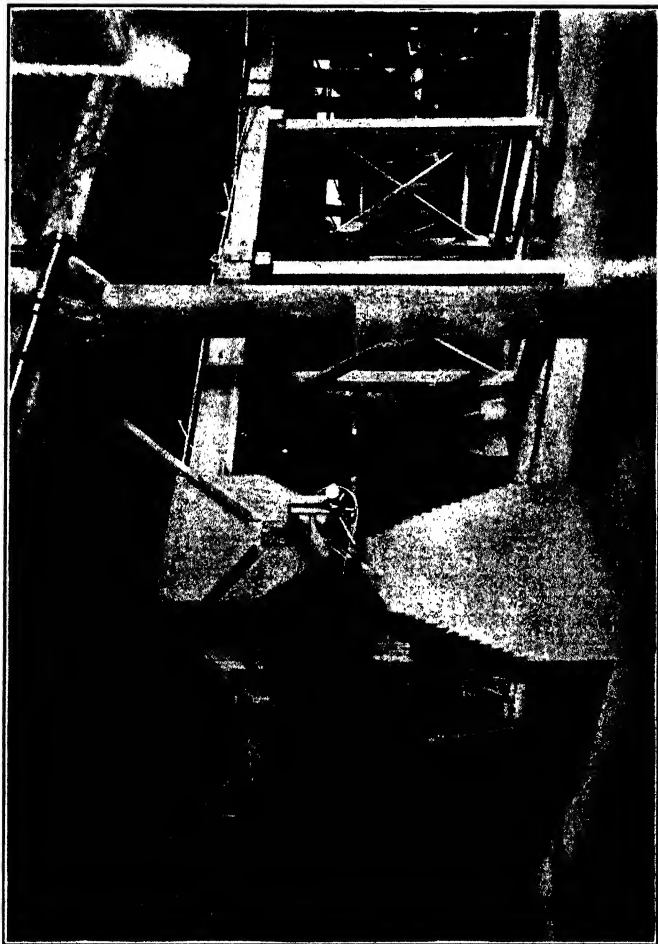


FIG. 35. — SEPARATING TANKS AND FLOAT TABLE — MILD PROCESS (ROWLEY).

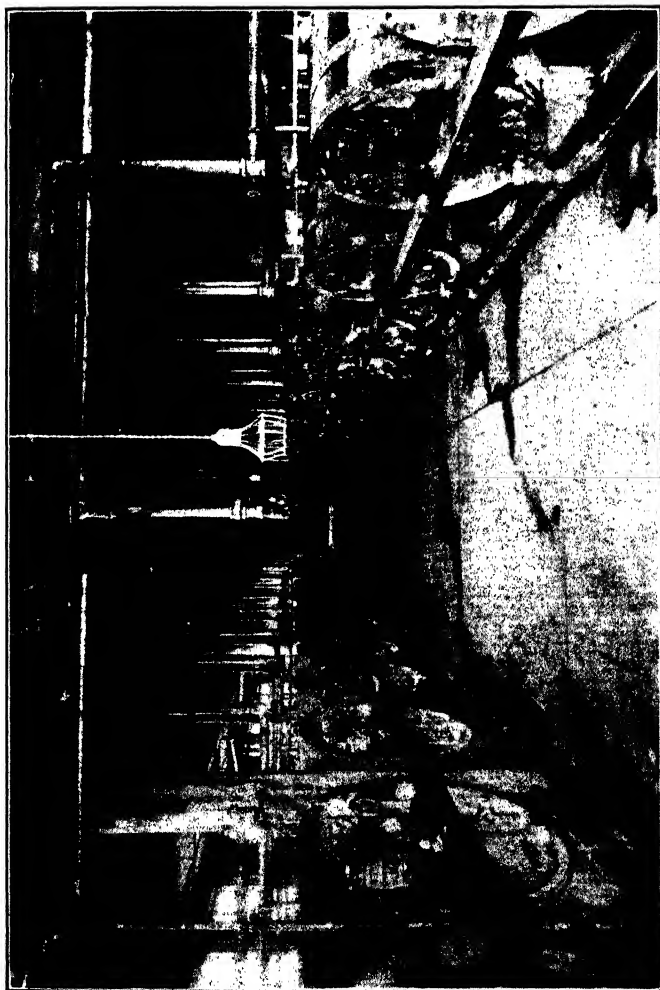


FIG. 36. — CARBONATORS. — MILD PROCESS (ROWLEY).

with the large apparent increase in volume, as it is possible by a long continued carbonation to form a very crystalline carbonate containing very little hydroxide, the operation being accompanied by a considerable diminution of apparent volume.

111. Advantages of Process. From a manufacturing standpoint this process has much to commend it, especially as regards the following items:

1. The process is not restricted to a specially refined lead.

2. It is under complete control.

3. It results in conversion into white lead of all of the metallic lead during the process, avoiding any metallic residues whatever.

4. The white lead produced is of a uniform grade — no tailings or sandy lead.

5. No mechanical losses of lead as the same water is used over and over again, there being no impurities of consequence present.

6. Manual labor is reduced to a minimum, the conveying of the material in the process being accomplished entirely by gravity and pumps.

7. The process can be made entirely sanitary as the workmen need not come in contact with the lead in any part of the process, nor is there any dust produced that contains lead particles, except in the final barreling operations.

8. Nothing is required in the manufacture, aside from the machinery, power and labor, that involves any expense except the cost of lead itself.

112. Not a Precipitation Process. The Mild process should not be confounded with any of the so-called precipitation processes, as it bears no analogy to them, the lead not being in solution at any stage of the process. As compared with other white leads, Mild process white lead is

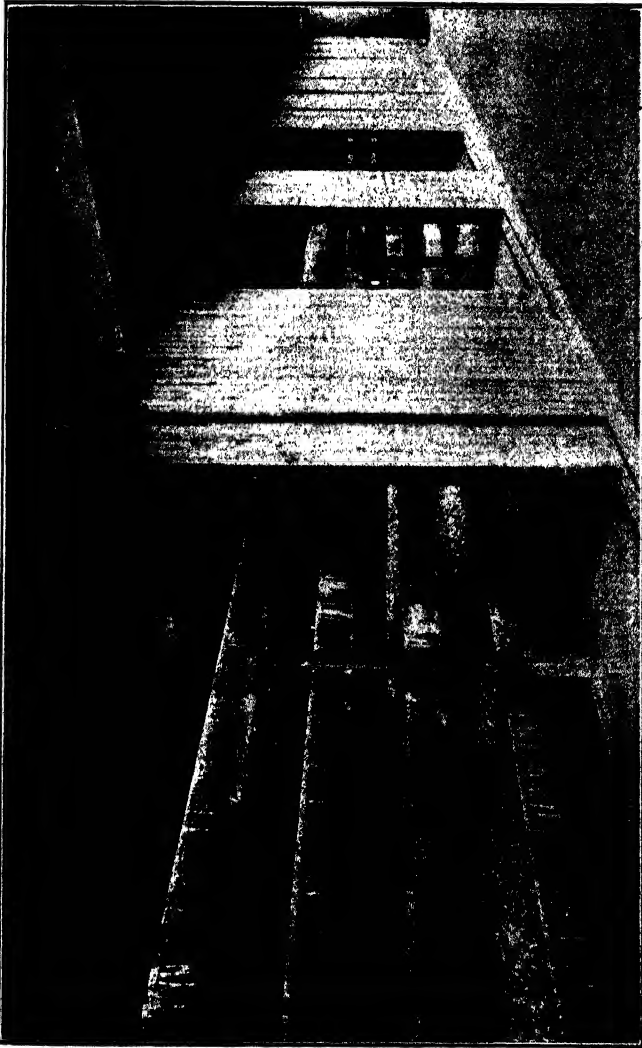


FIG. 37. — COPPER DRYING PANS. — MILD PROCESS (ROWLEY).

whiter than old Dutch white lead, being equal to Carter lead in this respect. The particles are of very uniform fineness, being slightly smaller than Carter, and much finer than old Dutch lead. Although very soft and chalky in appearance and "feel," it is as dense and does not require any greater quantity of oil in the grinding and little, if any, more in reducing to painting consistency, than old Dutch or Carter leads, and is sold in the same sized kegs. Under the brush it works easier, and owing to the uniform fineness of the particles, it covers more surface with an equal hiding power than any old Dutch process lead that the writer is familiar with.

CHAPTER IX.

MATHESON PROCESS.

113. Matheson white lead is the product of one of the newer methods of corroding, which are popularly but inaptly called "quick processes" in order to distinguish them from the older or Dutch process.

114. **Nature of Process.** In all of the so-called quick processes, the metal is reduced to smaller particles, and, therefore, exposes a greater surface to the action of the corrosive elements than is the case with the "buckle" used in the Dutch method, so that the corrosion of a given weight of metal is more quickly accomplished. However, the corrosion of so much lead as is exposed directly to the action of the corroding agents must progress substantially as rapidly in either method, and if the newer processes used the "buckle" instead of smaller units, their corrosion would be no quicker than by the Dutch method. Some of them, and notably the Matheson, would, however, still differ from the Dutch process in being practically continuous and permitting the recovery of the carbonate as rapidly as made, and to that extent they could justly be designated "quick" in contrast with the older method, in which more than one hundred days must elapse before the basic carbonate of lead, or white lead (which has been accumulating on the buckles as the water and acetic acid vapors and carbonic acid gas force their way through the outer layers of carbonate and continue to attack the inner core of metallic lead until they can no longer reach it) can be made available for marketing.

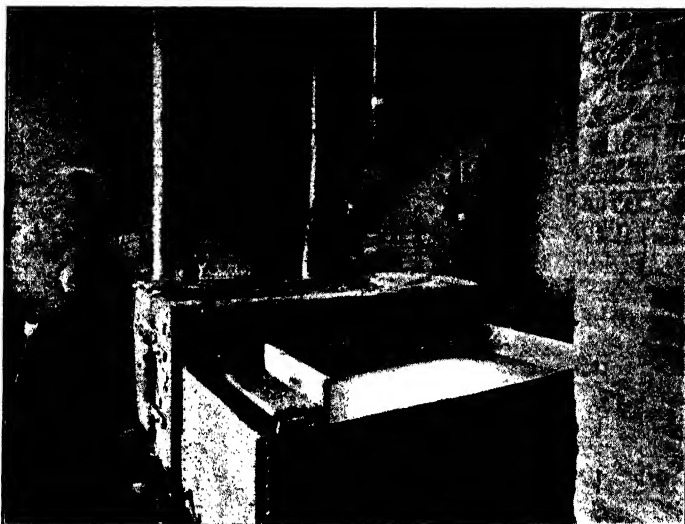


FIG. 38.—MELTING ROOM.—MATHESON PROCESS.



FIG. 39.—CORRODING TANKS.—MATHESON PROCESS.

115. Development in United States. Another point of difference between the Matheson process and some of the older methods is that it is more controllable, and can thus be made to yield a product more uniform than is obtained by those methods which are not open to inspection or regulation while they are working. The process itself is modeled upon some of the processes in use in France, but was modified by Mr. Ellert W. Dahl, a Norwegian chemist, who introduced it into this country in about 1893, and who for a number of years marketed his product here under the name "Premier White Lead." In 1898, it was purchased by the William J. Matheson Company, and has since been known under their name. The process has been subjected to some changes in its mechanical detail which have been developed on the larger scale upon which it has been manufactured, but the product upon analysis does not differ from its original composition, which conforms fairly closely to the accepted chemical formula for white lead, and its chemical behavior is comparative with that of any other hydrated carbonate of lead that is properly made.

116. Characteristics of Matheson Lead. Its physical characteristics are widely different, however, as it is whiter and finer, and is free from the gritty particles of the Dutch process, which are the result of the long exposure to continued action of the acid and gas, of the outer layers of carbonate formed on the "buckles." In specific gravity, Matheson lead is somewhat lighter than Dutch process, its bulk being correspondingly greater and its oil carrying power exceeding that of the heavier leads by about $33\frac{1}{2}$ per cent. In other words, 88 pounds of Matheson dry lead will require about 60 pounds of oil to put into the form of paint, properly reduced, and 92 pounds of Dutch process lead will require 45 pounds of oil to make a paint of equal consistency. The resultant product measures over $9\frac{1}{2}$ gallons



FIG. 40. — WASHING PRESSES. — MATHESON PROCESS.



FIG. 41. — SETTLING TANKS. — MATHESON PROCESS.

with Matheson lead, to less than 8 gallons of the Dutch, or about 25 per cent more volume of paint, which is claimed by the manufacturers to cover at least a correspondingly greater surface with equal opacity. It should be remembered, however, that the above increase in volume is due to the increased amount of oil used.

117. Manufacture. In the Matheson process, the metallic lead is "feathered," or brought into a form resembling a sponge in structure, by running the molten metal into water. This lead is brought into contact with dilute acetic acid in large corroding tanks or tubs. In the presence of air and steam a basic acetate of lead is produced, this, in turn, being transformed into hydrated carbonate by contact with carbonic acid gas obtained from coke furnaces. The carbonate is then repeatedly washed, after which most of the water is removed by filter presses, and it is then dried in vacuum driers. The whiteness of the lead results from its complete corrosion, and the consequent absence of "blue" lead in the carbonate, as well as to its freedom from tan-bark or other organic matter. The grinding process does not differ from that employed with other leads, except as to the greater amount of oil required, to which reference has already been made. Special precautions must be observed in freeing the white lead from residual acetates, which if not completely removed will be more than likely to give serious trouble when used in paints.

118. During the corrosion of the lead by this process, there is produced a considerable quantity of a crystalline practically insoluble basic acetate, which the author understands is separated and calcined into litharge, together with a certain amount of metallics which are difficult of conversion affording a most excellent grade according to the samples examined by the writer.

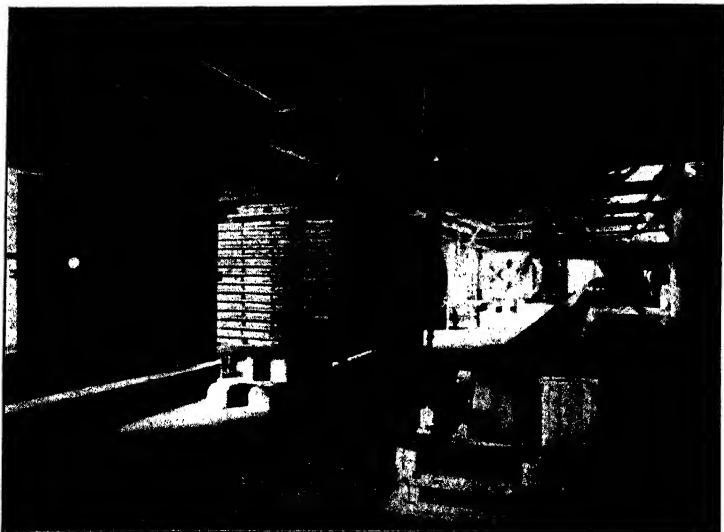


FIG. 42. — VACUUM DRIERS AND FILLING MACHINE. — MATHESON PROCESS.



FIG. 43. — PULP MILL. — MATHESON PROCESS.

119. Uses. Several examinations of Matheson lead by the writer have shown it to be quite uniform in composition, approximating 72.50 per cent carbonate to 27.50 per cent hydroxide. The product is of exceptional whiteness, and free from impurities other than basic acetates of lead. It not only takes a much larger amount of oil in grinding than other leads, but a much larger amount in reducing to painting consistency. For these reasons the writer understands that it finds its larger use in mixed paints and semi-paste goods, where these features are desirable, rather than as strictly pure lead in oil. Its hiding power or opacity is excellent when its spreading qualities due to the large amount of oil required are considered.

CHAPTER X.

THE SUBLIMED LEAD PIGMENTS.

120. Sublimed White Lead. The invention of sublimed white lead is due to Mr. E. O. Bartlett, who, while manager of the Keystone Zinc Company's works at Birmingham, Pa., in 1866, became impressed with the idea that a lead pigment could be made by the same process as that used for making zinc oxide, i.e., by sublimation of the ore in an oxidizing fire and collection of the condensed product in cloth filters or bags.

121. Early Development. In the latter part of the sixties he associated himself with the firm of John T. Lewis & Bros., of Philadelphia, for the purpose of carrying out experiments along that line. A small plant was built which was afterwards removed to Joplin, Mo., and enlarged under the financial backing of Mr. Lewis, and the experiments continued on a commercial scale. The location of Joplin was chosen because that city was in the heart of the enormously productive mining region of Southwestern Missouri, and also because the lead ores produced in that section were exceedingly free from other metals yielding volatile oxidation products which would contaminate the sublimate. The single exception was zinc which is, consequently, found as oxide in all sublimed white lead at present on the market to the extent of approximately five per cent.

122. The first patent for the process was taken out in 1870 and since that time there has been an almost continuous series of patents for improvements in the process

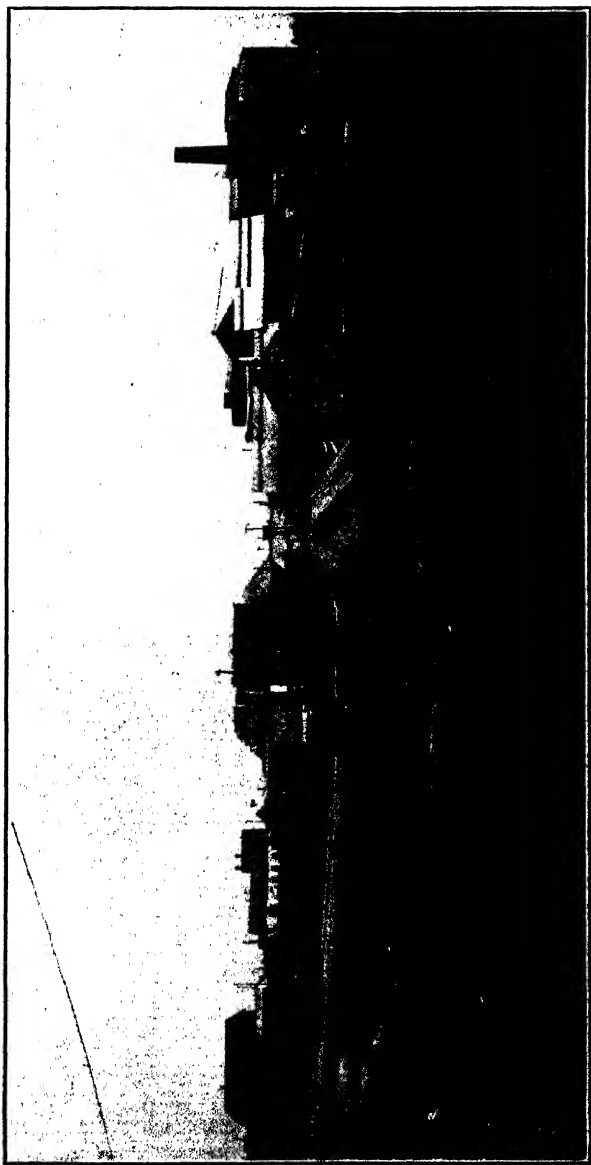


FIG. 44.—PICHER SUBLIMED LEAD WORKS.

taken out at short intervals. The pigment has been on the market commercially in this country for twenty-five years, although the quantity produced was relatively small until 1900. Since that date the production of sublimed white lead has rapidly increased.

123. Sublimation of the Ore. The ore used in the manufacture of sublimed white lead is a high grade of galena (native lead sulphide) which has been crushed and "jiggled" so as to free it from accompanying rocks. This separation is complete as regards interfering compounds, except, as mentioned above, in the case of zinc. The finely pulverized ore is fed into the furnace along with the necessary amounts of fuel and fluxes. The furnaces are of a special type which is a compromise between the furnace employed for zinc oxide and the blast furnace used in smelting roasted lead ores. The fire box has a circular water jacket supplied with tuyeres which inject a powerful hot-air blast from all sides. The intense heat generated instantly volatilizes the lead sulphide in gaseous form, which, as it rises from the incandescent hearth, comes in contact with the oxygen of the air from the blast, and at the enormously high temperature, is oxidized to what the manufacturers claim is an oxysulphate, which, after rising several feet in the cylindrical furnace lined with fire brick, passes into a large transverse brick lined flue.

124. Condensation of Fume. The heat of the combustion and oxidation is so great that the furnace and transverse flue or chamber are completely filled with flame and hence it is difficult to decide at just what point the combination is complete. After traversing this long horizontal chamber, the vapor or "white fume" as it is usually called, passes through a series of large air-cooled iron pipes or flues and through what are termed the "goose-necks," which are so arranged that the coarser particles

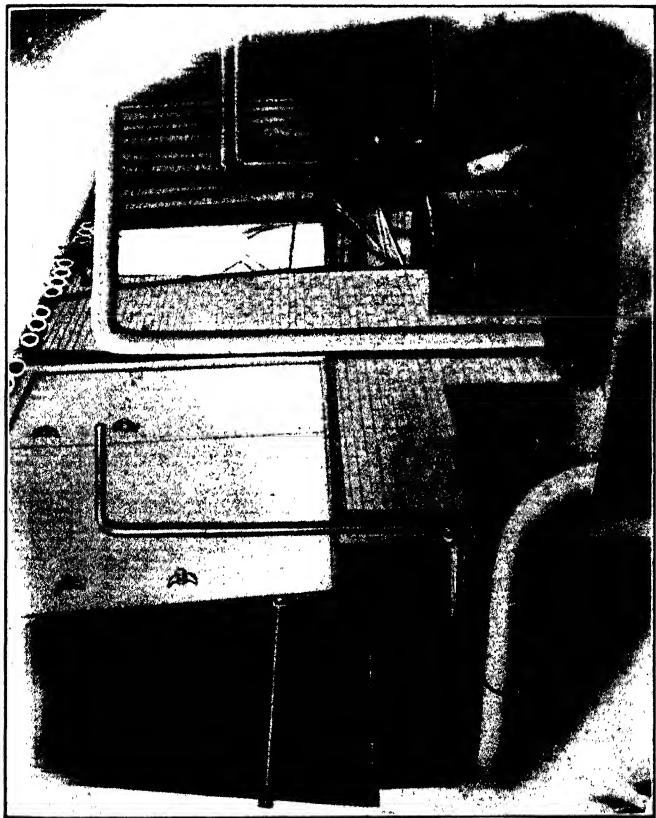


FIG. 45. — SUBLIMED LEAD FURNACES. — PICHER LEAD COMPANY.

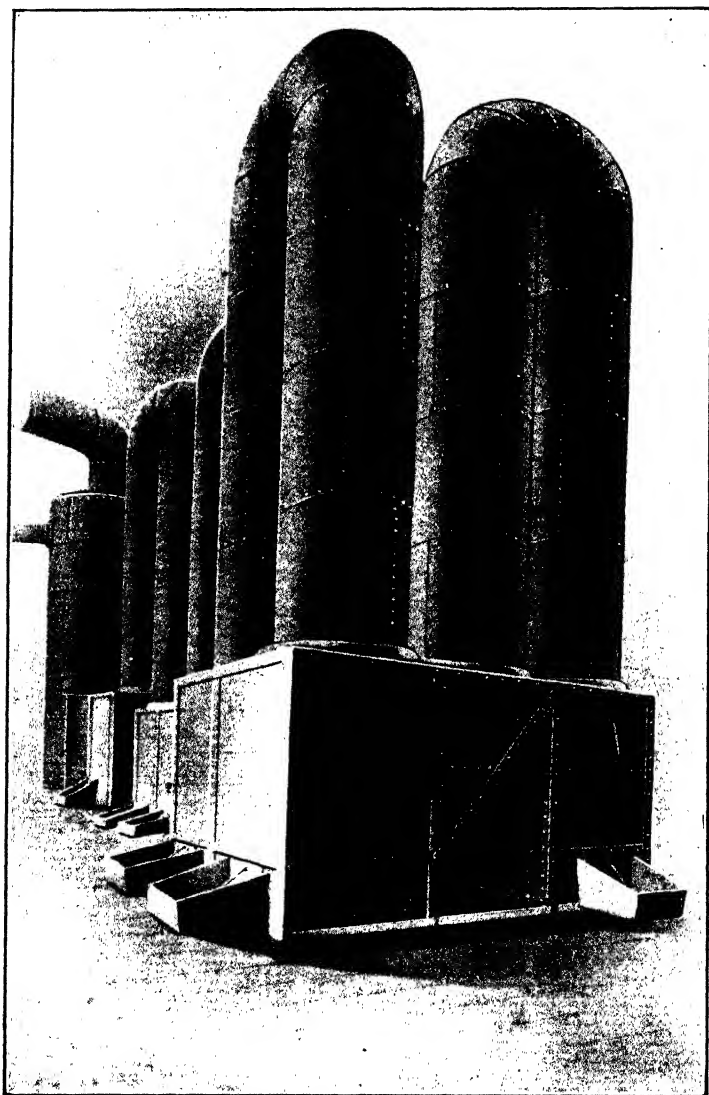


FIG. 46. — GOOSENECKS. — PICHER LEAD COMPANY.

containing impurities settle out and the "white fume" itself floats along, aided by powerful suction fans, for a total distance of between 700 and 1000 feet when the gases and "fume" are sufficiently cooled to permit of the collection of pigment particles in fabric condensers, allowing the gases to escape through their meshes.

125. Bag Room. The condensers or collectors are in the form of long bags, hung perpendicular in a large building known as the bag house. The bags are shaken at regular intervals to detach the pigment from the sides, the pigment collecting below the bags in large hoppers from which it is drawn into steel lined carts on the floor below and packed in barrels which hold about five hundred pounds. The atmosphere of the bag rooms is unbearable except for short intervals by reason of the sulphur dioxide in the escaping gases.

126. Uniformity of Product. Naturally, the ratio of the lead sulphate to lead oxide in sublimed white lead is dependent largely upon three factors, the nature of the ore fed into furnaces, i.e., whether it is entirely lead sulphide ore or whether other lead compounds are added; the amount of air which comes in contact with the ore; and the temperature at which the reactions take place in the furnace. These conditions being under control of the manufacturer, the product can be kept quite uniform and of the desired composition under favorable furnace conditions, although it is probable that atmospheric changes exert more or less influence on the nature of the finished product.

The range of variation in samples examined by the writer is as follows:

Lead sulphate.....	75 to 80 per cent
Lead oxide.....	20 to 14 per cent
Zinc oxide.....	5 to 6 per cent

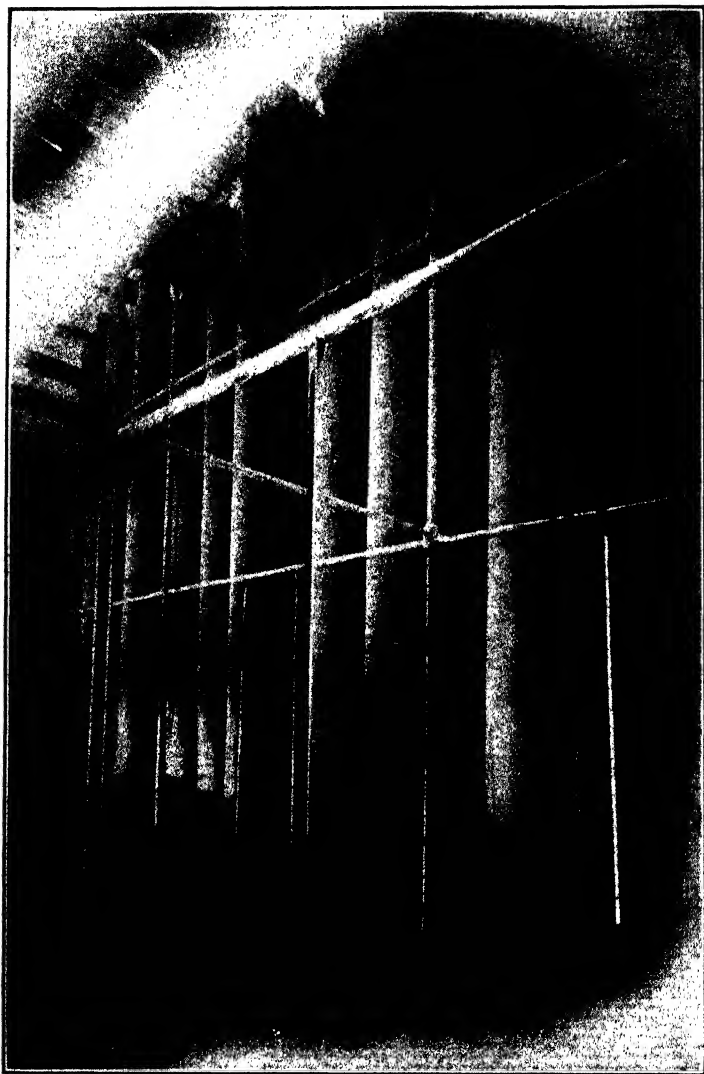


FIG. 47. — BAGROOM. — PICHER LEAD COMPANY.

127. Chemical Constitution. As heretofore stated, sublimed white lead is claimed to be a basic sulphate of lead. In substantiation of this claim it is argued that all of the lead oxides known to chemists are red or brown and a white oxide of lead is as yet unknown; further, that a mixture of sublimed white lead in oil dries normally in about the same length of time as required for corroded white lead, — two days, — while a mixture of lead sulphate, litharge (lead monoxide) and zinc oxide, in the same proportions as those shown by an analysis of sublimed white lead, dries in from ten to twelve hours. Recent work by Chevalier indicates that the fume from a furnace roasting lead sulphide has the formula $Pb_3S_2O_9$, apparently a complex of two molecules of sulphate with one of oxide. The conditions of the production of the two fumes are not essentially different and it is claimed by the sublimed white lead makers that they have isolated this compound in a state of purity although not on a commercial scale. If the existence of this basic sulphate is a fact, then commercial sublimed white lead is a mixture of it with a varying amount of neutral lead sulphate.

These arguments, while presumptive, can hardly be accepted as entirely conclusive. The reactions and combinations that take place at exceedingly high temperatures are but imperfectly understood and it is entirely possible that we may have aggregates formed at high temperatures in which the components are so intimately associated that they are apparently chemically combined without such actually being the case.

128. Yearly Production. Many improvements have been made in the process of manufacture during the past few years, which have resulted in an increased demand for sublimed white lead on the part of the paint manufacturers as shown by the table on page 117.

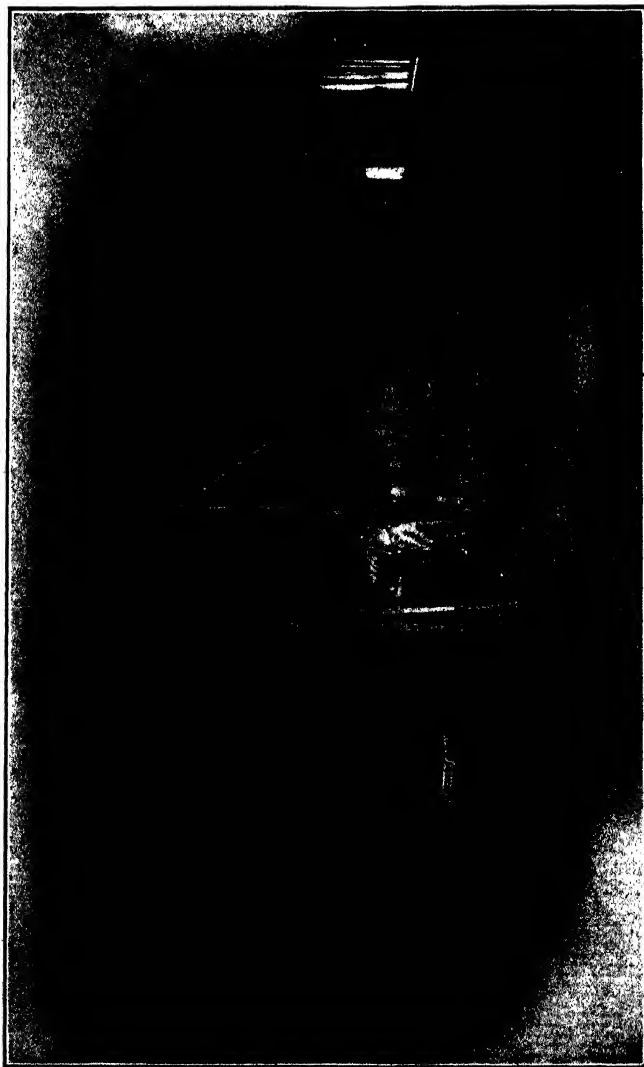


FIG. 48. — COLLECTING HOPPERS. — PICHER LEAD COMPANY.

Year.	Production in pounds.	Value.
1902	9,465,500	\$449,611.00
1903	8,592,000	386,640.00
1904	12,954,000	550,589.00
1905	13,954,000	732,585.00
1906	15,974,000	958,440.00
1907	17,400,000	1,026,600.00

129. Physical Characteristics. As prepared at the present time, sublimed white lead is a very finely divided substance entirely amorphous in structure. In color it is not quite as white as a good white lead. This may in part be accounted for by the fact that it contains about 0.06 per cent of ferric oxide. Its specific gravity is slightly less than corroded white lead, being 6.2. The average diameter of the particles is about one thirty-five thousandth of an inch while those of white lead vary in the same sample between one four hundredth and one fifteen thousandth of an inch. It is for this reason, probably, that paints made wholly or largely of sublimed white lead show brush marks more plainly than white lead paints. It requires more oil in grinding than ordinary white lead but not sufficient to give it excessive spreading qualities.

130. After having once been packed together in barrels, it is much less poisonous than corroded white lead; which fact is not of so great moment as formerly because with modern appliances for ventilation in the manufacturing and painting establishments and increasing cleanliness on the part of the workmen, lead poisoning has largely ceased to be the formidable evil that it once was in this country.

131. Uses of Sublimed White Lead. Because of the exceeding fineness of its particles, sublimed white lead is seldom ground straight in linseed oil but it is generally ground with other pigments, and hence finds its largest

use in the manufacture of mixed paints; and because this fineness allows the pigment to remain in suspension in the vehicle, it is a favorite constituent for dipping paints. Owing to its comparative inertness to sulphurous vapors and gases and having a hiding power substantially equal to white lead, sublimed white lead is rapidly coming into extensive use in railroad specifications. It is also finding a wide use in the structural iron and steel paints.

132. Chalking. The objections frequently urged against this pigment are that it chalks, that it is not equal in whiteness to white lead, and that paints containing it thicken up and work stiff and greasy in cool weather or during the cooler portions of the day. While chemist at North Dakota Experiment Station, the writer was closely associated with Professor E. F. Ladd in the conducting of a large number of practical exposure tests in which sublimed white lead was applied straight and in a number of combinations. As a result of these and other practical tests the writer believes that sublimed white lead does chalk even more, possibly, than old Dutch process white lead, but the chalking is of an entirely different character. When ordinary white lead begins to chalk vigorously, it will be found that the paint film has lost its elasticity, and has become brittle and friable throughout; also, that the luster of the film under the chalk-like coating has entirely disappeared. A sublimed white lead film, on the other hand, retains much of its original elasticity under the chalk coating, indicating that the disintegration is confined to the surface, and it is possible that the retention of the "chalk" on the surface gives some protection to the unaffected coat below. When used with other pigments, the chalking of sublimed white lead is retarded and it behaves almost exactly like old Dutch process white lead under similar conditions.

133. Comparative Whiteness. Sublimed white lead, when applied straight, is not of equal whiteness as compared with old Dutch white lead, having a slightly yellowish, creamy tone. After one year's exposure, however, the result is reversed. The sublimed white lead is then the whiter and has lost its creamy tint; while the old Dutch process white lead has taken on its customary grayish tone.

Paints containing a large percentage of sublimed white lead, according to the experience of the writer, show a distinct tendency to thicken and work stiffer under the brush during cool weather. This may be due to the exceeding fineness of the particles. If so, the change is physical rather than chemical and hence not a serious matter when handled understandingly by the master painter and when it is considered that most painting is done in warm weather.

134. Inertness toward Tinting Colors. Due to the chemical stability of sublimed white lead, it has little injurious effect on the tinting colors which it may be ground with: as is well known, chrome yellow, chrome green, Prussian or Chinese blue and some organic colors do not give permanent tints when ground with white lead, due to chemical interaction between the color pigment and the white lead. Addition of chemically inert pigments lessen the action in the case of white lead but do not entirely inhibit it. For this reason sublimed white lead has come widely into use in mixed paints, especially in the tints replacing a portion of the white lead and thus increasing the permanence of the tint.

SUBLIMED BLUE LEAD.

135. Sublimed blue lead is a pigment finding considerable use as a protective coat for metallic surfaces. Its manufacture is by methods analogous to those employed for the manufacture of sublimed white lead, but in this case the sublimation is conducted in a reducing instead of an oxidizing atmosphere.

136. Properties. Because of the large amount of unsaturated sulphur compounds which it contains, the sublimed blue lead coat is quite different from that of any other paint made with linseed oil. Apparently the sulphides and sulphites contained in it affect the oil so that, after drying, it is comparatively immune from action by coal gas. However useful the presence of these ingredients may be after the coat is applied, they are a considerable detriment in the eyes of the paint maker, as this material has a very great tendency to cause the paint to thicken, or liver, if allowed to stand after being thinned. For this reason, sublimed blue lead is not, as a rule, sold straight in liquid form, but is packed either as paste or else ground with a percentage of graphite or red lead.

137. Composition. In composition, sublimed blue lead varies somewhat, but the analysis is about as follows:

	<i>Per cent.</i>
Lead sulphate	50
Lead oxide	35
Lead sulphide	5
Lead sulphite	5
Carbon	3
Zinc oxide	2
	<hr style="width: 10%; margin-left: auto; margin-right: 0;"/> 100

The production, in 1907, was 2,422,000 pounds, valued at \$135,632.

SUBLIMED LEAD OXIDE.

138. Sublimed lead oxide is a sublimate obtained as a by-product from the manufacture of litharge by the hearth or cupellation process. It is an exceedingly fine, sulphur-yellow material, and desirable for many purposes, particularly color making.

Unfortunately, it is not, as yet, produced as a regular article of commerce on a large enough scale to attract attention, although litharge manufacturers are working toward this end.

CHAPTER XI.

WHITE LEAD MANUFACTURE IN EUROPE.

139. Comparative Costs of Manufacture. The manufacture of white lead in England and on the Continent is conducted in a much different manner than in this country. The majority of European white lead plants are much smaller than the average plants in the United States, and, especially in England, are conducted on a much more conservative scale with regard to labor-saving machinery and appliances; so, notwithstanding a lower European wage scale, American white lead plants undoubtedly enjoy a lower cost of production. Government regulations safeguard as carefully as possible the health of the employees, whereas in this country there are substantially no restrictions, although there is at the present time a manifest tendency to legislate in this direction.

140. English Regulations. The following abstracts from the English regulations (1906), in addition to those quoted in the chapter on White Lead Poisoning, will afford some idea of the safeguards placed around the employees who work with lead products.

“No dry lead color shall be placed in any hopper or shoot without an efficient exhaust draught and air guide, so arranged as to draw the dust away from the worker as near as possible to the point of origin.”

“Every person employed in a lead process shall be examined once each calendar month by the certifying surgeon of the district, who shall have power to suspend from employment in any lead process.”

“Overalls shall be provided for all persons employed in lead processes, and shall be washed or renewed at least once every week.”

“No person shall be allowed to introduce, keep, prepare, or partake of any food, drink (other than medicines provided by the occupier and approved by the certifying surgeon) or tobacco in any room in which a lead process is carried on.”

141. In England, the majority of white lead plants operate under the old Dutch process, although there are one or two plants which make use of modifications of the German Chamber process, which process will be discussed in a subsequent portion of this chapter. The Bischof process, used at Mond's Works at Brimsdown in Middlesex, has recently attracted considerable attention. The metallic lead is converted into an oxide by a simplified process and is then heated to 250 to 300° C., in a current of water gas, which reduces the lead to a black suboxide of unknown composition, which is treated with water, a yellow hydrate being formed and considerable heat being evolved. The hydrate is then converted into white lead by treatment with carbon dioxide gas.

142. **English Methods.** Many of the details of the old Dutch process, as carried out by the English, differ considerably from the practice in this country. Instead of using round buckles and placing them inside of the corroding pots, the more usual English practice is to cast the lead into sheets or gratings, which are laid on top of the pots, which are much smaller than those in use in this country. The building of the stacks, which usually have a height of twenty-two to twenty-four feet, is usually done by women, who work barefoot, and who convey the tan-bark in baskets carried on their heads (see frontispiece). The lead is usually handled by cranes. The work of taking down the



FIG. 49.—BUILDING THE STACK. — ENGLISH METHOD.

stacks is performed by men only, who wear a regulation costume (see Fig. 50), required by the Home-office to be worn by all workers in the white lead departments. The white lead must also be dampened before its removal from the stack is attempted. This is in marked contrast with the practice in this country, where any sort of a costume is permitted, and in the several factories visited by the writer no attempt was made to keep down the dust in the stack operations.

143. Characteristics of English White Lead. As found on the market, English white lead in oil is much stiffer than the American product; this is due to the different method of grinding, where, instead of rotary buhrstone mills, powerful granite rolls moving at different speeds are used. The several English brands examined by the author showed evidence of most careful corrosion, resulting in great purity of color, almost theoretical chemical composition, and freedom from crystalline or sandy lead. Newcastle-on-Tyne is one of the principal seats of manufacture. Other important corroding centers are London, Glasgow, Chester, Bristol and Sheffield.

144. German Chamber Process. The more progressive German manufacturers use a modification of the Dutch process, which materially shortens the length of time required by the other process. The present method is probably an outgrowth of what was used at Klagenfurth, in Carinthia, for a great many years, dating back perhaps as far as 1835. White lead made by this process enjoyed a remarkably high reputation. This presumably was due, not so much to the method of manufacture, as to the very great purity of the lead used, which was produced from the mines at Bleiberg.

145. Klagenfurth Modification. The principal points of difference between the old Dutch process and the Klagen-

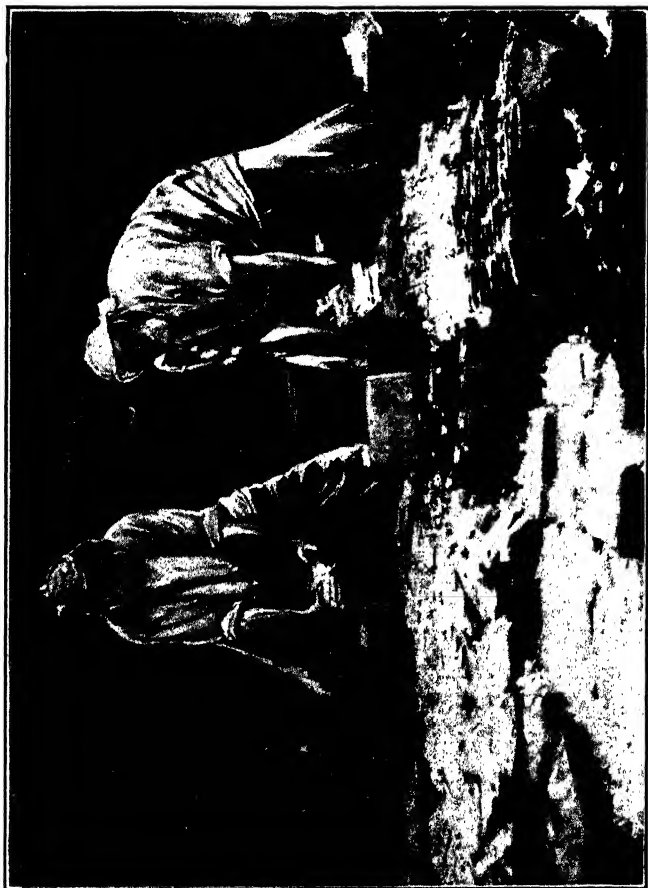


Fig. 50.—TAKING DOWN THE STACK. — ENGLISH METHOD.

furth modification consisted in the vaporizing of the vinegar or acetic acid by artificial heat and the production of the carbon dioxide by the fermentation of substances other than tan-bark or horse manure, usually grape skins or refuse from wine manufacture, the corrosion being effected in large closed chambers about one hundred feet in length, each chamber being divided into upper and lower compartments by a loosely constructed floor, through which warm air from below could readily pass. The lower compartments contained the furnace with flues leading to the room above. On the floor of the upper compartment were placed strongly constructed boxes containing the acetic acid or vinegar, and the fermenting material, such as grape skins, grape pulp, etc.

146. Above each box was a framework extending to the roof, containing numerous cross pieces, over which the sheets of lead were placed. The warm air from the furnace below, warming the contents of the boxes, not only vaporized the acetic acid, but also effected a vigorous fermentation of the grape pulp, liberating considerable amounts of carbon dioxide, which, with the water vapor arising with the acid, afforded all the requisites of the Dutch process. The lead being cast into considerably thinner sheets than was customary in the older process, and with a much more vigorous action of the corroding agents resulted in the shortening of the time of corrosion to six or eight weeks. The resulting white lead, after being freed from metal residues, ground, washed and dried, afforded a product of great whiteness, as this process assured entire absence of hydrogen sulphide with the attendant blackening of the lead.

147. **Present German Methods.** The present German chambers process may be regarded as the result of the gradual development of the Klagenfurth method, the

vaporization of the acid and the generation of the carbon dioxide being under direct control by the operator. The corroding rooms or stacks are approximately thirty feet long, twenty feet wide and fifteen feet high, the walls being covered with earthenware tiles for resisting the action of the acid vapors. The stacks are fitted with racks from which the strips of cast lead are hung as in the Klagenfurth process, six to eight tons being the usual stack charge.

148. The acetic acid is supplied in the form of vapor by evaporating diluted vinegar in iron covered pans set in brickwork, the vapors being conveyed in earthenware pipes to the stacks and distributed throughout the rooms by means of large perforated pipes.

The carbon dioxide is produced by burning coke or charcoal in iron stoves, care being taken to secure as complete combustion as possible, the resulting gas being introduced into the stacks through the perforated pipes that disseminate the acid vapors, thereby securing a uniform mixture of acid and gas.

149. Effecting the Corrosion. The formation of an amorphous basic carbonate of lead, substantially free from neutral carbonate or crystalline carbonates, by the chamber process depends on the formation of a true basic acetate on the sheets of lead before the conversion into carbonate is begun. In order to secure the most desirable conditions, great care must be exercised in regulating the amounts and strength of the acid admitted, in the introduction of proper quantities of air, and in maintaining the proper temperature in the stack room. During the first twenty-four hours, acetic acid of five to six per cent strength may be distilled into the stack room; the second twenty-four hours the strength should be reduced to about one per cent, in order to prevent a too vigorous action on the lead due

to the increased warmth of the chamber. On the third and following days the strength of the acid should be further reduced, depending on the conditions observed in the stack. 0.5 to 0.7 per cent strength represents the more usual practice.

150. When distinctly perceptible drops of dissolved basic acetate have formed on the lead sheets, carbon dioxide should be admitted and the supply of atmospheric air reduced correspondingly. The formation of white lead proceeds rapidly, and in a short time the strips of lead are covered with a white coating. The best results are obtainable by introducing the acetic acid, water vapor, and carbon dioxide in such amounts as will maintain a damp or slightly pasty feeling to this coating, necessitating entrance to the chamber at regular intervals, which, owing to the high temperature, often 60° to 80° C., will require the use of protective clothing and a means of artificial respiration on the part of the examiner.

151. Rapidity of Corrosion. As before stated, the success of the operation depends on the formation of a basic acetate of lead first, which is converted into basic carbonate and neutral acetate by the carbon dioxide and air. The neutral acetate reacts in turn with the metallic lead, forming more basic acetate with the assistance of the water vapor, which is converted into a further quantity of white lead or basic carbonate with a further quantity of carbon dioxide, more neutral acetate being formed. This cyclic reaction explains the diminution of acetic acid vapor required after the process is well under way.

152. The corrosion will be most rapid near the inlet openings for the vapors in the chamber and, therefore, the action will be completed near the bottom and center of the room before the strips near the walls and upper portion of the chamber are more than one-half or two-thirds corroded;

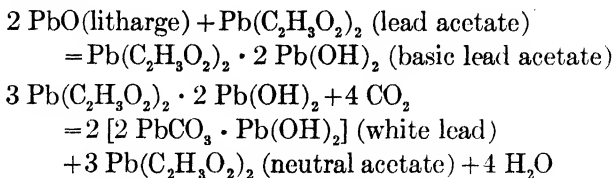
and, in order to secure the most desirable grade of white lead, the operation is stopped before complete conversion is secured in all parts of the chamber in order to avoid over-corrosion, entailing conversion into crystalline carbonates on the strips most vigorously acted upon. Under improved conditions the operation requires five to seven weeks, eighty to ninety per cent of the metallic lead being converted into white lead. The crushing, screening, grinding and washing operations are entirely similar to those in the old Dutch process.

153. Lack of Success in United States. Although the chamber process has been very successful in Germany and in the adjoining countries, attempts at introduction into the United States have failed entirely. Two reasons may be assigned for this; first, lack of intimate knowledge on the part of the promoters of all the fine points to be observed in controlling the corrosion, resulting in a product not at all uniform in composition, while, on the other hand, the long experience of the German chamber manufacturers has enabled them to control the details of their process successfully; second, lack of economy of the chamber process as compared with the Dutch process in this country, the latter undoubtedly being on a much more economical basis here than in Europe.

154. In Montreal, Canada, a white lead plant has recently been built which operates under a modified form of the chamber process, and as there is only one other white lead in Canada, it should at least be moderately successful.

155. The French, or Thenard's Process. The practicability of this process was first demonstrated about 1801 by Thenard, a French chemist, who discovered that if carbon dioxide was passed into a saturated solution of basic lead acetate that white lead or basic carbonate of

lead was precipitated and a certain amount of neutral lead was regenerated which could again be converted into basic acetate, the process being exemplified by the following equations:



156. The lead acetate may be obtained by treating granulated lead with acetic acid in the presence of air or by treating litharge with acetic acid; the latter method is easier and more rapid but the higher price of litharge offsets these advantages. The carbon dioxide must be used in a more concentrated state than in the chamber process and is usually prepared by heating limestone with burning coke in a specially constructed furnace and is forced into the solution of basic acetate under a slight pressure. The precipitation usually requires about ten to twelve hours. After removal, the white lead is washed thoroughly to free it from acetate salts. The product obtained is of exceeding whiteness, but, owing to a somewhat crystalline nature, has less opacity or hiding power than white lead made by the other processes. For this reason and because of the comparatively high cost of production, this process has not come into the general use that was formerly anticipated. The Matheson process, which is a much improved modification of the Thenard principle, is the only one of this type in successful operation in this country.

157. Present French Practice. In fact, Thenard's process has practically passed out of use, the old Dutch process having taken its place. The procedure of the French, old

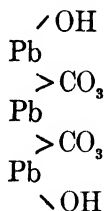
Dutch process corrodors is very similar to that of the English. In some factories the lead is cast in sheets and then rolled into a spiral, which is placed inside the pot; in other works, the lead is cast in the form of gratings which are placed on top of the pots. While the majority of French factories have discarded manure for tan-bark, a number of the more conservative plants still depend on horse manure as the source of heat and carbon dioxide, as the corrosion is completed in nearly half the time required by tan-bark. The grinding, washing and drying operations correspond closely with the English practice.

CHAPTER XII.

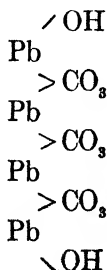
PROPERTIES OF WHITE LEAD.

158. Composition. White lead of accepted grade is a white, earthy, heavy amorphous powder which appears under the microscope to consist of round globules of irregular size. White lead prepared by the newer processes is usually whiter than that made by the Dutch process.

159. Chemically, it may be considered as a basic carbonate of lead. The best grades of white lead approximate very closely the formula $2 \text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, which may be graphically represented as follows:



According to this formula, there are about sixty-nine parts of lead carbonate to thirty-one parts lead hydroxide. This constitutes an increase of about twenty-five per cent of white lead on the basis of the metallic lead used. In other words, 100 pounds of metallic lead produces approximately 125 pounds of white lead. There are, however, other basic carbonates of lead, among which is $3 \text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, represented by the graphic formula:



160. The Higher Carbonates. These higher carbonates increase the yield of white lead, and there is a notable tendency, especially with the newer processes, to work in this direction, as the added increase may amount to from one to two per cent of the weight of the pig lead used. This gain, however, is at the expense of the opacity, as the higher carbonates possess less hiding power. White lead which has been overcorroded will be more or less crystalline instead of amorphous, due to the presence of the crystals of the normal carbonate. Such leads are markedly inferior in their hiding power.

161. Ageing of White Lead. The ageing of white lead, both in the dry state and in oil, has been a fruitful subject for discussion. As to the precise nature of the changes undergone, but little information that is really satisfactory is obtainable. That certain changes take place in both cases is undeniable, as an experienced painter can almost invariably pick out an aged lead from among unaged leads of similar manufacture. The author has observed that a tank of wet white lead not quite up to standard whiteness will, on standing for eight to ten weeks, improve materially in whiteness. This change is apparently due to molecular rearrangements tending to a uniform relation between hydrate and carbonate, and is apparently assisted by the pressure due to the weight of the contents of the tank.

162. Salvadori¹ is of the opinion that the ordinary basic carbonate is fully as stable, if not more so, than the normal carbonate, and that the latter is easily converted into the former by boiling with water or even by heating under water for several hours at 70° C. It is certain, however, that under other circumstances a reverse action will take place resulting in the formation of a crystalline

¹ *Gaz Chim Ital.* 34, 87.

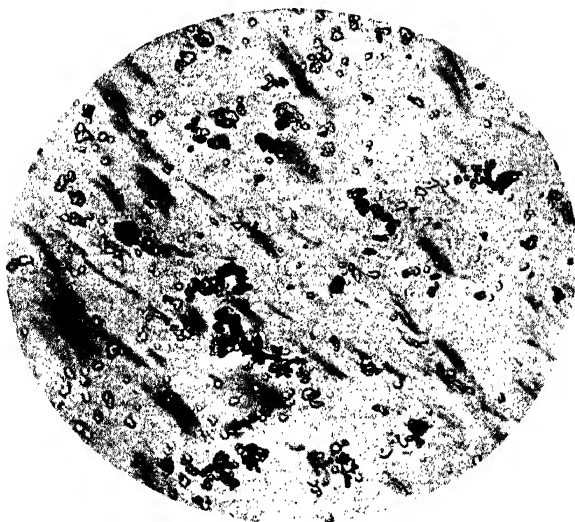


FIG. 51. — OLD DUTCH PROCESS WHITE LEAD.
Magnification 500 diameters.

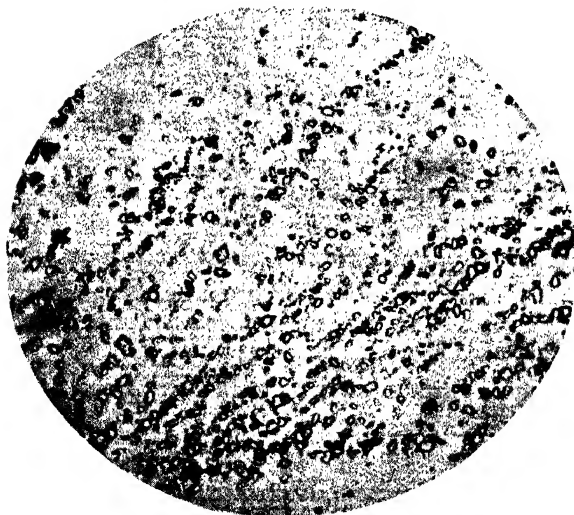


FIG. 52. — MILD PROCESS WHITE LEAD.
Magnification 500 diameters.

normal carbonate. From these operations, however, and remembering that pressure is a powerful aid to chemical transformations, it is not at all strange that a substance of as complex a nature as white lead, in bulk either wet or dry, will undergo various molecular rearrangements which an ordinary chemical analysis will not indicate.

163. Free Fatty Acids. In the case of white lead ground in oil, the problem is complicated by the temperature and pressure of grinding and the amount of free fatty acids contained in the linseed oil. Such changes as will occur under these conditions will reach a consummation much more rapidly, probably, than in the previous instances, and these changes probably terminate within a few weeks after the lead has been ground.

164. Fineness of Particles. White lead varies greatly with regard to the fineness of the particles of which it is composed. Mild process white lead particles are uniformly fine, while old Dutch process white lead is composed of fine and comparatively coarse particles intimately mixed. The following table prepared by the Paint Manufacturers' Association,¹ gives some idea as to the size of the various pigment particles under average conditions of grinding.

No.	Name.	Diameter in inches.		
		Small.	Average.	Large.
1	Dutch process lead.....	.00002	.00007	.00026
2	Quick process lead.....	.00002	.00012	.00018
3	Picher lead.....	.000014	.00007	.00014
4	Zinc oxide.....	.00002	.00007	.00014
5	Zinc lead.....	.000014	.00007	.00014
6	Beckton white.....	.00003	.00007
7	Barytes.....	.00006	.00036	.0021
8	Gypsum.....	.00014	.00044	.0022
9	Blanc fixe.....	.00003	.00014	.0003
10	China clay.....	.00009025
11	Abestine.....	.0001549

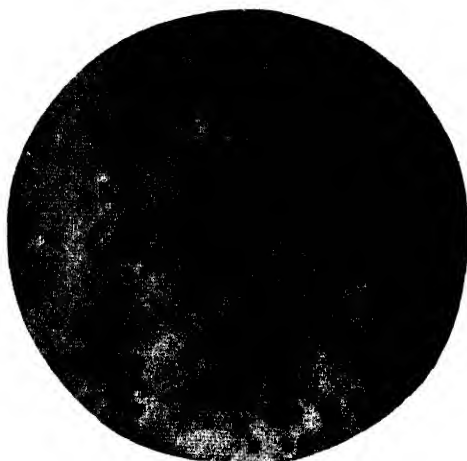


FIG. 53. — PRECIPITATED WHITE LEAD.
Magnification 500 diameters.



FIG. 54. — SUBLIMED WHITE LEAD.
Magnification about 500 diameters.

165. Action of White Lead on Linseed Oil. Much has been written concerning the action of white lead on linseed oil. Hannay and Leighton, in the Proceedings of the Chemical Society, No. 124, have questioned the frequently made statement "that saponification takes place when white lead is ground with linseed oil, giving rise to peculiar working properties, which other pigments do not have. They show that no such combination between the lead and oil takes place, and that a very small trace of oleate of lead in the oil will cause serious blackening under the influence of the small amount of sulphuretted hydrogen in the air, when pure white lead would hold its color, showing that such saponification would be decidedly deleterious."

166. The conclusion drawn was that dry white lead produced slow oxidization, but no saponification of the oil, since saponification implied hydrolysis, and could only take place in the presence of moisture.

A. H. Hooker confirms these statements, and calls attention that "in wet or pulp ground leads alone we find a partial saponification to take place and that such lead is vastly more susceptible to the blackening influence of sulphuretted hydrogen than ordinary lead."

167. Stability of White Lead toward Heat. White lead is not a very stable pigment. It begins to lose its combined water at 110 to 130° C. Several of the quick-process leads break down much more easily than old Dutch process lead. By keeping the temperature below 150° C., all of the combined water can be driven off in six to eight hours, with very slight loss of carbon dioxide.

168. A slightly higher heat breaks down the white lead at once into an oxide, high temperature giving litharge, and a continued lower temperature an oxide which absorbs oxygen, forming the product known as orange mineral, which may be considered a debased form of red lead. In

actual practice the crystalline tailings or sandy lead is largely used for this purpose.

169. Reactions with Acids. Owing to the weakness of the chemical linkage between radicals composing white lead, it is extremely susceptible toward acids and alkalies, being readily soluble in acetic and nitric acids, and hot hydrochloric acid, the lead chloride formed separating out on cooling. Hence when hydrochloric acid is used as a solvent for lead compounds in mixtures, such solutions should be filtered boiling hot, else crystals of lead chloride will form in the pores of the filter paper, which will be dissolved out with difficulty, even with boiling water. Sulphuric acid converts lead compounds into an insoluble sulphate. This operation is much made use of in the quantitative analysis of lead compounds. However, in the presence of even slight amounts of nitric, hydrochloric or acetic acids the lead sulphate is sufficiently soluble to introduce quite a serious error in the determination. The addition of alcohol will overcome this difficulty to a considerable extent, although it is best to expel any free nitric, acetic, or hydrochloric acid by evaporation.

170. Solubility. Solubility of lead compounds in 100 c.c. pure water at room temperature:

<i>Compound.</i>	<i>Grams Soluble.</i>
Lead Carbonate.....	0.00011
Lead Sulphate.....	0.00410
Lead Chromate.....	0.00002
Lead Chloride.....	1.08
Lead Acetate.....	50.0
Lead Nitrate.....	56.0

171. Action of Sulphur Compounds. As is well known, white lead is easily attacked by sulphuretted hydrogen and gases containing sulphur compounds, pulp ground leads being more susceptible than leads previously freed from

water before being ground in oil. This blackening or darkening is one of the leading objections to its use as the base of white paints. In fact, for interior work, but little strictly pure lead is used; generally a mixture of zinc oxide and white lead is used, in which the zinc oxide is in preponderance, as the effect of sulphur compounds on zinc oxide is not noticeable, zinc sulphide being white. In cities where large quantities of soft coal are burned, the darkening of white lead is especially rapid. This is due not only to the sulphurous gases in the atmosphere, but also to the soot particles which lodge on the comparatively rough surface of the lead paint film, and through the agency of moisture, the sulphur and other corrosive substances in the soot act directly on the paint film.

172. Chalking of White Lead. The principal objection brought against white lead as a paint pigment is that it "chalks or flours." This chalking may begin within four months after application or may not be apparent at the end of twelve to fifteen months. Many reasons have been ascribed for this defect, for defect it is, of white lead. In many instances the oil is undoubtedly at fault, especially oils which either by treatment or long standing have become high in free fatty acids, and will cause a rapid disintegration of the paint film. Again, the temperature at which the lead is ground in the mill has much to do with its chalking. The low temperature at which white lead begins to break down certainly renders any undue heating of the mill a serious consideration. Many grinders even to-day are using uncooled buhr mills. Even with a water-cooled mill operated as efficiently as possible, it is often difficult to keep below the danger temperature, especially after the mills have been running six or seven hours. In many instances the result is so pronounced that the lead hardens in the package within 36 hours after grinding.

173. Effect of Residual Acetates. Another important cause of chalking, and one that the author believes should merit special attention on the part of chemists, is the presence in greater or less quantity of acetate of lead, which is to be found in all white leads made through the instrumentality of acetic acid. In numerous tests which have come under the observation of the writer, white leads prepared without the use of acetic acid "chalk" very much slower, and to a much less extent than the other leads. That these more or less basic acetates of lead exert an influence all out of proportion to the amount present seems certain. In fact their action may be regarded as of a catalytic nature, and the author is firmly convinced that many abnormal cases of "chalking," if carefully traced, would have shown the presence of an abnormal quantity of acetate of lead present in the white lead used.

174. Protracted Oxidation. It is also a well-known fact, as Hooker states, "that white lead promotes the slow oxidization or drying of the oil and the ultimate product of this oxidization is a dry powder without life or elasticity. White lead hastens this end of completed drying much more rapidly than any other pigment, except of course red lead and litharge, and so unless some means is used to retard the action, the oil perishes and the dry lead alone is left to wash or chalk off. However, the chalking of white lead while objectionable is not entirely so, since it leaves the surface in an excellent condition to receive a fresh coat of paint."

175. White Lead Specifications. One of the best specifications that has come under the observation of the author covering the use of white lead is the one in use by the Rock Island Lines of the St. Louis and San Francisco Railroad Company. The following are the points covered:

176. "**Material.** White lead must be furnished in paste form and must contain nothing but oil and pigment, in the following proportions by weight:

Oil, not less than 7 per cent nor over 10 per cent.

Pigment, not less than 90 per cent nor over 93 per cent, the paste to contain not over one per cent by weight of volatile matter, at 212° F., and must be free from skins and mix readily for spreading, and when made into a paint it must not be deficient in opacity, and must be of maximum whiteness, work freely under the brush, and when thinned down ready to use it must not settle into a hard mass on standing overnight."

177. "**Oil.** The pigment must be ground in pure linseed oil, well clarified by settling and age, and must otherwise meet the requirements of this company's standard specification for raw linseed oil.

"**Pigment.** The pigment desired is the pure, fully-hydrated basic carbonate of lead, which must not be crystalline in structure or contain more than 0.15 per cent acetic acid, and must approach closely the following composition:

Lead carbonate, not less than 67 per cent nor over 80 per cent.

Lead hydrate, not less than 20 per cent nor over 33 per cent.

"The pigment must not contain more than one-half of one per cent of lead sulphate."

178. The only objection the writer would raise against these requirements is the high per cent of carbonate permitted. Seventy-six per cent should be regarded as the highest desirable amount, as above this point the lead begins to lose in opaqueness or body.

CHAPTER XIII.

LEAD POISONING.

179. The English White Lead Commission. In England, and also on the continent, especially in France, there has been a very pronounced agitation against the manufacture and use of white lead as a paint pigment, due to the alleged harmful effect on the employees of the white lead works and the painters who use the product. This agitation led to the formation of the White Lead Commission in England, in 1898, whose report was instrumental in introducing many improvements in the industry. In France the white lead industry has been made the object of special legislation restricting and regulating the sale and use of white lead.

180. Lead Poisoning in United States. In the United States the question of white lead poisoning has remained practically unnoticed. To the casual reader this may seem strange, but when we compare the condition of the industry abroad and at home, the reasons why it has attracted so slight attention at once becomes apparent.

Two reasons primarily may be advanced as an explanation for this state of affairs:

1. Superiority of American methods and workmen.
2. Absence of female labor in this industry in America.

181. In the United States the white lead, after having been ground in the water mills and subjected to the usual washing, is pumped on large copper steam-heated drying pans, some of which are nearly one hundred feet in length by nearly ten or more feet in breadth, while in England

until very recently the thick paste was placed in large earthenware bowls which were carried by women to drying compartments known as "stoves," which were essentially rooms heated by a stove or steam coils and provided with a large number of shelves arranged around the sides. Until 1898, the "filling" and "drawing" of the stoves was very largely done by women, and, as Sir Thomas Oliver¹ has pointed out, this part of the process "has been the cause of a larger number of severe and fatal cases of lead poisoning than any other department in a white lead factory." "The work was found to be so detrimental to female life that the White Lead Commission recommended that no woman or girl should be allowed to work in the stoves." At the present time while the use of copper drying pans is becoming more common in England and on the continent, the practice has by no means become universal.

182. English Regulations. In 1899, the Chief Inspector of Factories issued special rules for white lead works. These were modified again slightly in 1901, and the following are the essential requirements as stated in Factory Acts of 1901.

183. Duties of Occupiers. 1. No person shall be employed in drawing Dutch stoves on more than two days per week.

2. No woman shall be employed or allowed in the white beds, rollers, washbecks, or stoves, or in any place where dry white lead is packed, or in other work exposing her to white lead dust.

3. The occupier shall provide and maintain sufficient and suitable respirators, overalls and head coverings, and shall cause the same to be worn.

4. A supply of a suitable sanitary drink, to be approved by the appointed surgeon, shall be kept for the use of the workers.

¹ Dangerous Trades, page 289.

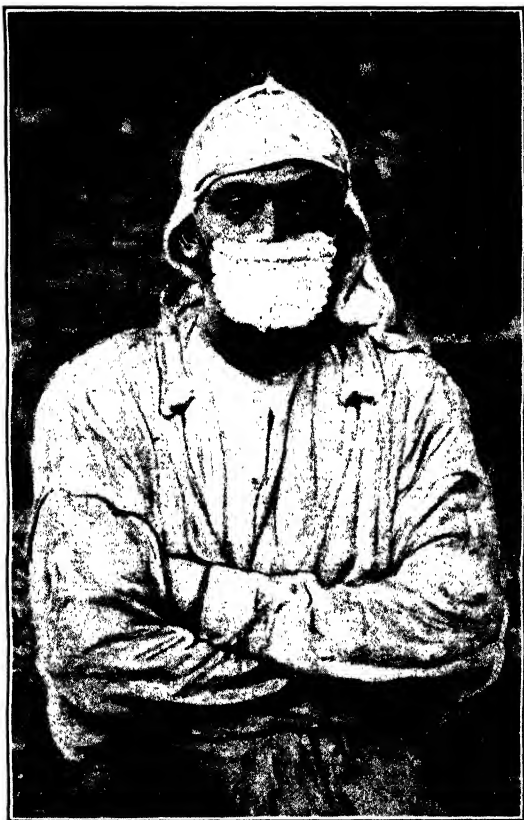


FIG. 55. — REQUIRED COSTUME OF ENGLISH WHITE LEAD WORKER.

5. The occupiers shall provide and maintain lavatories for the use of workers, one lavatory basin for every five persons employed, to which must be supplied a constant supply of hot and cold water.

6. Before each meal, and before the end of the day's work, at least ten minutes in addition to the regular meal times should be allowed to each worker for washing.

7. The occupier shall provide and maintain sufficient baths and dressing-rooms for all persons employed in lead processes, with hot and cold water, soap, and towels, and shall cause each such person to take a bath once a week at the factory. A bath register shall be kept containing a list of all persons employed in lead processes, and an entry of the date when each person takes a bath.

184. Duties of Persons Employed (Briefly Stated). 1. No person, after suspension by the appointed surgeon, shall work in a lead process without his written sanction.

2. Every person employed in a lead process shall take a bath at the factory at least once a week, and wash in the lavatory before bathing; having done so, he shall at once sign his name in the bath register with the date.

3. No person employed in a lead process shall smoke or use tobacco in any form or partake of food or drink elsewhere than in the dining-room.

4. No person shall obtain employment under an assumed name, or under any false pretenses.

185. English Statistics. That these regulations adopted in 1899 were justified is amply shown by the official reports on lead poisoning for the three years preceding.

<i>Year.</i>	<i>Cases.</i>
1896	357
1897	370
1898	480

These figures indicate that one in every seven to eight employees suffered from lead poisoning. The drying stoves furnished two and one-half times as many cases of plumbism as the corroding beds.

186. Precautions Adopted by the French. In France even more rigid precautions are prescribed against lead poisoning than in England. Those in use at the corroding works of M. Expert-Besançon may be taken as representative of the care exercised with French white lead workers. As the best preventative of plumbism, regular rations of milk are prescribed which the workmen are required to take at six o'clock and nine o'clock in the morning and three o'clock in the afternoon. To the nine o'clock ration is added hyposulphite of soda, about one and a half pounds to the gallon. It is also to be noted that the workmen are not permitted to drink their milk or partake of food in any of the rooms where any lead products are handled or are in process. The men are required to wash their face and hands and rinse out their mouths before eating or drinking their milk and on leaving the factory at the close of the day. Frequent baths are also required. The time required for all of these operations is considered a part of the day's work and for which the workmen are paid.

187. As a final precaution each workman is inspected at least once a week by a doctor who keeps a complete record of the health of each man. When indications of lead poisoning are observed, cessation from work is ordered by the doctor until recovery is complete, at which time a certificate is issued permitting him to return to work.

188. Recent Improvements. Since 1901, conditions have materially improved in England, as in 1900 the total cases notified in the Northeastern Division of England was 197, in 1901 there were 98 cases notified, and in 1902

only 69 cases were notified. On the Continent methods have been introduced to some extent for incorporating the lead with oil without drying out the water, similar in principle to the white lead pulping mills used in this country, thus avoiding danger from white lead dust common to this part of the process. In this country mechanical barrel packers and the strict use of respirators have reduced this danger to a minimum, there being much more lead sold dry than abroad.

189. The taking down of the corroding beds is perhaps the most dangerous part of the process in this country, as it is an operation in which manual labor cannot with advantage be supplanted by mechanical devices. The incorporation of the dry lead oil by means of "chasers" is also a serious source of lead poisoning, unless, as is the practice in some plants of placing the chasers in small rooms, the workmen remaining outside until the incorporation of the lead and oil is complete.

190. Restrictive Legislation. Even when all reasonable precautions have been adopted, there is always danger of the employees acquiring lead poisoning in a corroding plant, especially one in which the old Dutch process is used, but in the opinion of the writer the danger is not nearly serious enough to warrant restriction by legislation against the manufacture and use of white lead. While it is true that painters suffer more or less from lead poisoning, it is usually due to lack of even ordinary cleanliness, for the painter who is scrupulously neat is very seldom affected. Much of the complaint regarding the various forms of kidney diseases with which many painters are troubled, especially those working under cover, is due essentially to the irritating and toxic effect of the turpentine used. Carriage painters are perhaps more seriously affected by this class of troubles than any others, and yet the

amount of white lead applied by them is very small as compared with the amount applied by the ordinary house painter.

191. Danger to Women. The different forms and manifestations of lead poisoning, such as "wrist drop," "lead colic," are more or less well known, but the more serious aspects which this affliction may assume should be more generally known and recognized, and effectual measures taken to prevent development into a chronic or acute stage. The effect of lead poisoning is very much more serious on women than on men. This has been amply demonstrated by Oliver,¹ who states that "where the two sexes are as far as possible equally exposed to the influence of lead, women probably suffer more rapidly, certainly more severely, than men." "Children of female lead workers almost invariably die of convulsions shortly after birth or during the first twelve months. If the child is the offspring of parents both of whom are lead workers, it is puny and ill nourished, and is either born dead, or dies a few hours after birth." Fortunately in this country female labor is not employed in white lead factories.

192. Symptoms of Lead Poisoning. In discussing white lead poisoning, Oliver states in the same connection, that: "The symptoms of plumbism are manifold. Usually easy of recognition, they are sometimes so obscure as to render the malady difficult of detection, even by a careful physician. One of the earliest signs is pallor of the countenance. There is developed a degree of anæmia which gradually increases until the features become altered and expressionless, a form of bloodlessness which, since it is characteristic of lead poisoning, is spoken of as Saturnine cachexia. This becomes very pronounced, so that it is easy to recognize lead workers by sight. A few weeks' work will transform a

¹ Dangerous Trades, pages 301, 303.

healthy-looking, florid young woman or man into a pallid and listless individual. During the time that the pallor is developing, the individual often complains of a disagreeable metallic taste in the mouth, especially on rising in the morning, and of a distaste for food."

193. "The reason why colic is such a common and early symptom of saturnine poisoning is because the alimentary canal is one of the principal channels by which lead enters the system, and lead is known to have a special affinity for muscular fiber and nerve tissue, and to induce spasms. Colic is often attended by vomiting and by obstinate constipation. The pain is of varying degrees of severity. Sometimes it is so mild that the individual is able to follow his occupation, but in discomfort. At other times it is so severe that he rolls about in agony, and is with difficulty kept in bed. After recovery most of those who have been ill return too early to employment. One attack of plumbism unfortunately predisposes to another. On examining the mouth of a lead worker there is usually to be seen a bluish line along the margin of the gums close to the teeth. The gums are ulcerated, and in the case of an old lead worker they are retracted, and thus expose a considerable length of the fang."

194. **Effect on Nervous System.** It is upon the nervous system that the worst effects of lead are seen. Usually after having experienced one or more attacks of colic, but sometimes without these, a lead worker suddenly or gradually loses power in his hands and fingers. His hands become paralyzed, hang powerless by his side, and the patient is said to be suffering from "wrist drop." In "wrist drop" the extensor muscles of the fingers and wrists rapidly waste. As a rule, the affection is painless, but in some instances the loss of power is preceded by muscular tenderness. The muscles of the shoulders and

upper arm, too, may be affected, or the weakness affects the muscles of the foot, and causes "ankle drop."

195. Chronic Lead Poisoning. There still remains the chronic type of lead poisoning "in which the individual, after having been exposed for a lengthened period to the influence of lead, and having experienced one or more attacks of colic, indicating that his system is becoming impregnated with lead, is never well; he is profoundly anæmic, is the subject of frequent headache, imperfect vision, and incomplete wrist drop. Albumen is present in the urine, and there is a slight degree of dropsy of the face, hands, and feet, — physical signs that point with these just mentioned to structural alterations having occurred in the kidneys, liver, heart, and blood-vessels, retina and nervous system. Life drags on from day to day, only to end in a lingering illness, or it is brought to a sudden close either by uræmic convulsions, or in consequence of rupture of a blood-vessel in the brain."

196. Absorption Through the Skin. Many authorities consider that the inhalation of lead dust or its introduction into the system through the mouth is far more dangerous than ordinary contact with the skin, as, for example, the hands and arms. The author, however, believes that the danger of absorption through the skin has been much underestimated. In one corroding plant with which the author was intimately acquainted, over twenty-five per cent of its workmen in one year received medical treatment for lead poisoning, the large majority of whom never came in contact with any perceptible amount of lead dust; and as they were required to wash thoroughly before eating, the amount introduced through the mouth was very slight. The liberal use of heavy paraffine oil on the hands and arms did much to alleviate the absorption, and immediate improvement was noticed.

CHAPTER XIV.

MANUFACTURE OF ZINC OXIDE.

197. Ancient History. This pigment which occupies such a prominent position in the paint world to-day was practically an unknown paint material sixty years ago. Yet, while its rise into favor has been so rapid and recent, it has been known to scientists for many hundred of years. In fact, its history extends as far back as that of white lead, for Pliny mentions it under the name of *cadmia* when describing the sublimate of impure zinc oxide found in the chimneys of the brass foundry furnaces. Discorides also states that in the manufacture of brass "pompbox is formed like tufts of wool." The later alchemists spoke of this characteristic formation of zinc oxide as *lana philosophica*. The similarity between the oxide of zinc, obtained by the combustion of metallic zinc, and snow led the alchemists to name it *nix alba*.

198. Production on a Commercial Scale. Unlike white lead, zinc oxide was of little or no practical use to the ancients, and the industry remained undeveloped. One of the first suggestions as to its adaptability as a paint pigment was made in 1781 by a French chemist, who discovered the process of converting zinc into oxide on a commercial scale, and advised its use instead of white lead, but with no especial results. And it was not until the time of LeClaire the famous French contractor and painter in 1847 that zinc oxide came into commercial use as a pigment.

199. Work of LeClaire. LeClaire, wiser than the major-

ity of reformers, turned public prejudice against itself. His contracts called for the use of pure white lead, and while he believed in the superiority of zinc oxide he recognized the futility of attempting to convince the public by any ordinary means. He therefore interpreted his contracts rather liberally, and used zinc oxide instead of white lead. "The superior beauty and durability of his work rapidly increased his trade, and when he felt his position sufficiently strong, he turned the prejudice of his patrons against themselves by painting here and there in each new building a certain section with pure lead. At the end of a short period the lead naturally began to change color and to 'chalk off,' and the inferiority of these portions promptly attacked criticism. When LeClaire was ready, he proclaimed the facts, with the final result that to-day zinc holds an absolutely unassailable position in France. LeClaire received honors and medals in profusion, and the government conferred upon him the order of the Legion of Honor."

200. LeClaire's Process. The LeClaire process of manufacturing zinc oxide consisted of volatilizing the metallic zinc in a retort, the resulting zinc vapors being mingled with currents of air and burned, the zinc converted into the oxide which was collected as a white powder in a series of flues and chambers; his process being the precursor of the present "French Process." The factory of LeClaire is still in operation. The high cost of the product prevented its coming into general use until after the elaborate investigations of the French Government which resulted in its being required in all government work.

201. Present French Process. The Société Anonymé de la Vielle Montagne is the largest producer of zinc oxide by the French process in Europe, producing in the neighborhood of 8000 metric tons yearly, equivalent to 8820

English tons. The metallic zinc or spelter is volatilized in a special form of retort; the vapor issuing from the retort is oxidized in the presence of a current of air, and after passing through a series of pipes is collected in long settling chambers provided with hopper bottoms through which the collected oxide may be removed. The purity of the oxide, especially as regards whiteness, depends much upon the distance it is carried in the settling chambers before deposition, and the product is graded accordingly; the two leading brands being Vielle Montagne Green Seal and Red Seal, the former being the better quality and commanding the higher price.

202. Composition. The composition of the Vielle Montagne zinc oxides varies according to Ingalls as follows:

Zinc oxide	99.695 to 99.995 per cent
Lead oxide	0.200 to .002 per cent
Cadmium oxide	0.100 to .000 per cent
Ferric oxide	0.005 to .003 per cent

The manufacture of zinc oxide from the metal is also an important industry in Silesia, the production being in the neighborhood of about one thousand metric tons. As the Silesian zinc always contains lead which converted into oxide gives a yellowish color to the zinc oxide, carbon dioxide from burning coke is introduced into the distilling retort which converts the lead into carbonate, according to Ingalls. The zinc oxide is collected in large upright bags similar to the American practice. The largest works in Silesia is the Antionenhütte.

203. The cost of production of zinc oxide from the metal is considerably higher than that of zinc oxide produced direct from the ore, as is the common practice in this country, but it insures the absence of certain objectionable impurities like cadmium, which is considerably more vola-

tile than zinc, and produces a brown oxide which would cause a discoloration of the finished product if it were not removed in the process of the manufacture of the metal. As the majority of European ores contain cadmium, a direct process similar to that used in this country is out of the question.

204. Processes in Use in the United States. In the United States the larger part of the zinc oxide produced is derived from the ore. The Florence, Pennsylvania, plant of the New Jersey Zinc Company, however, manufactures zinc oxide from the metal by what is substantially the French process, the metallic zinc being heated in retorts, volatilized, and the vapors burned to the oxide which is drawn into collecting chambers by the draught from a high chimney. The material so collected is treated to further purify it and improve its color. The greatest care must be exercised in the selection of the metal used and in all of the subsequent steps of the process, but when properly operated this process produces the purest white pigment known. The product is graded in a manner similar to the *Vielle Montagne*, and is known under the name of *Florence Green Seal* and *Florence Red Seal*.

205. The Work of Jones and Wetherill. The invention of the American process for the manufacture of zinc oxide is ascribed to Samuel T. Jones, who constructed a furnace for this purpose in 1850. The process was materially improved and placed on a commercial scale by Col. Samuel Wetherill in 1855, who worked with the *Franklinite* ores of New Jersey. The growth of the industry was somewhat slow at first, but after 1880 it developed rapidly and constitutes to-day one of the largest of the metallurgical industries. Unlike the manufacture of the white lead pigments, the zinc oxide industry has shown comparatively few improvements in the process of manufacture during the last

thirty years. While the principles of the process have remained unchanged, there has been a marked improvement in the character of the ore sent to the oxide furnaces, which is now first given a roasting to drive off the large amount of the sulphur, because when the oxidation of the sulphides and the volatilization of the zinc is accomplished in one process in the same furnace, the collected oxide is contaminated with appreciable amounts of zinc sulphates and a considerable amount of sulphur dioxide remains occluded in the oxide particles, which is a serious consideration from the paint manufacturer's point of view.

206. Zinc Oxide Plants in the United States. At the present time there are four plants engaged in the manufacture of commercially pure zinc oxide, and they are located in the States of New Jersey and Pennsylvania. These plants are operated by the New Jersey Zinc Company. Another plant is located at Mineral Point, Wisconsin, and operated by the Mineral Point Zinc Company, which is affiliated with the New Jersey Zinc Company. The zinc oxide produced at this plant, however, contains varying quantities of lead sulphate, and is graded accordingly. Other zinc oxide plants are located near Joplin, Missouri; Coffeyville, Kansas; and at Canon City, Colorado; but as the pigments produced at these plants contain a large percentage of lead sulphate, the procedure in these plants will be considered separately.

207. Development of the New Jersey Zinc Mines. The development of the New Jersey zinc mines constitutes a very interesting chapter in the development of our mineral resources. The mines at Sterling and Franklin were discovered in the latter part of the eighteenth century, it is said, by a party of Swedish miners who were traveling overland from Baltimore to New York. Some ore is supposed to have been sent to England about this time, but we find no

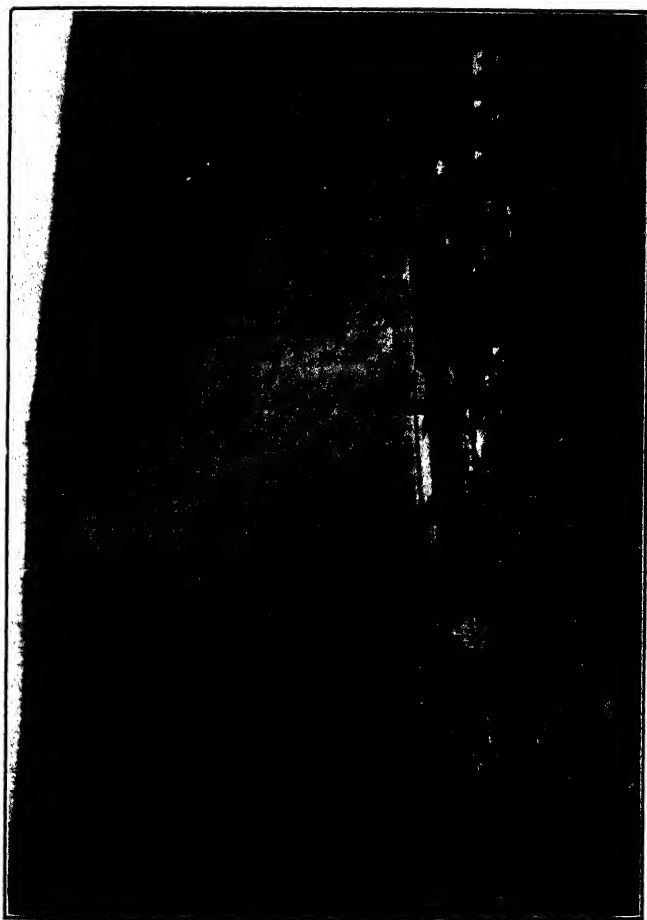


FIG. 56.—PALMERTON WORKS. — NEW JERSEY ZINC COMPANY'S BLAST FURNACES, POWER HOUSE AND OXIDE PLANT.

record of its having been received or treated. In any case, the mines were known to exist as early as 1824, when Messrs. Van Uxen and Keating described some of the minerals. The first mining done at Franklin was when the United States Government made the standard weights and measures. They imported some workmen from Belgium, built a spelter furnace at Washington, and made the zinc partly of ore from Franklin and from scattered boulders of ore found in Sparta Valley, and partly from ore from Perkiomen, Pennsylvania. The old pit from which this ore was taken was known as the "Weights and Measures Opening," and was in existence until about 1900, when the mining operations caused its disappearance. No further mining was done until 1848, when the mines at Sterling Hill were opened. Mining did not begin at Franklin until a couple of years later.

208. At first an attempt was made to manufacture spelter from the ore, but this was not successful, and the manufacture of oxide of zinc was started at Newark. At first the ore was worked in reverberatory furnaces, and the product was of a rather poor quality, and the cost extremely high. Later the ore was treated in muffles by a process said to have been discovered by Mr. Farrington, the Superintendent of the works, but which was identical with one patented by Atkinson in England, April 2, 1796. Still later the present method of manufacturing oxide of zinc direct from ore was discovered and patented by Col. Samuel Wetherill.

209. **Controversy regarding the Ownership of the Deposits.** At the time that mining operations were first started in Franklin, the mineral rights had been sold to two different companies by Col. Samuel Fowler, who owned the Mine-Hill farm, on which the principal deposit is located. In the first deed he conveyed all the gold, silver, copper,

lead, zinc and other ores and minerals containing gold, silver, copper, lead and zinc, except the metal, mineral, or ore known as Franklinite when it exists separate and apart from the zinc, and in the second deed he conveyed all the mineral rights that had been reserved in the first deed. The ambiguous nature of these conveyances led to litigation, which lasted almost continuously from 1854 to 1897, and was only concluded when the present New Jersey Zinc Company acquired the title to all mineral rights in the Mill-Hill farm. The reason that the deeds were made in this way was that at that time it was believed that there were two separate veins, one consisting almost entirely of Franklinite, and the other of other zinc minerals. Subsequent work has proved that this was not the case, and the point to be decided by litigation was whether the vein, which is a mixture essentially of the minerals Franklinite, willemite, zincite and calcite, was "Franklinite separate and apart from the zinc," or "zinc."

210. Composition of Franklinite Ore. The Franklin ore ¹ of New Jersey, from which the larger portion of our zinc oxide is produced, is a complex ore composed of Franklinite, willemite, and calcite in varying proportions, together with occasional quantities of zincite, tephroite, garnet, fowlerite, and a few other minerals. As it comes from the mines the ore varies widely in composition, but the following will serve as an example:

	<i>Per cent.</i>
Iron sesquioxide	32.06
Manganese protoxide	11.06
Zinc oxide	29.35
Calcium carbonate	12.67
Silica and insoluble matter	14.86
	100.00

¹ Mineral Industry, -1893, page 673.

211. These figures may be calculated to the following mineral composition:

	<i>Per cent.</i>
Franklinite.....	51.92
Willemite.....	31.58
Calcite.....	12.67
Zincite.....	0.52
Tephroite and other silicates.....	3.31
	100.00

212. The specific gravity of these minerals is as follows:

<i>Name.</i>	<i>Specific Gravity.</i>
Zincite.....	5.43-5.70
Franklinite.....	5.00-5.09
Tephroite.....	4.00-4.12
Willemite.....	3.89-4.18
Calcite.....	2.50-2.77

213. **Chemical Composition.** The chemical composition of these minerals is about as follows:

Zincite, sometimes spoken of as "red zinc ore," is when pure, oxide of zinc, containing 80.3 per cent metallic zinc. It is frequently contaminated with manganese.

Franklinite is a complex mineral found in almost inexhaustible quantities in New Jersey. It contains about 66 per cent oxide of iron, 12 per cent oxide of manganese and 22 per cent oxide of zinc.

Willemite is zinc silicate containing about 73 per cent zinc oxide and 27 per cent silica.

214. **Preliminary Treatment of the Ore.** The ores are usually crushed and concentrated at the mines before shipment. The concentrates, which consist of the zinc minerals in a fairly fine state of division, are treated at the oxide works about as follows: The ore is mixed with about



FIG. 57. — PALMERTON WORKS. — OXIDE FURNACES. — LENGTH OF BUILDING 1780 FEET.

one-fifth its weight of high grade anthracite coal, and charged into fire-brick lined revolving furnaces heated by producer gas, the ore being heated to bright redness. The ore, after passing through the furnace, is discharged into a cooler, from which it goes to the storage bins.

215. When the ore is required for use, it is passed over magnetic separators and jigs into five products. The first of these consists of the magnetic minerals, mainly Franklinite. This is all used for making oxide of zinc and gives the best quality produced. The second product is called half-and-half and consists of the less magnetic minerals of the ore. This is also used for making oxide of zinc, but not being as pure as the Franklinite gives a smaller proportion of the higher grades. The third product is willemite from the jigs, which is used for making spelter or metallic zinc. The fourth product is the tailings from the jigs, which is thrown away. The fifth product is the fine dust from the ore, which is removed before separating. This is also used in the manufacture of oxide of zinc.


216. The Oxide Furnaces. The furnace used for this purpose is  shaped in section, with a flat iron grate about four feet wide and ten feet long above a closed ash pit. The grate is composed of heavy iron plates about six inches wide, lying close together, each plate being perforated with a large number of small holes through which air is blown at a pressure of two to four inches water-gauge. The roof of the arch over the grate is of fire-brick. The doors at each end of the furnace are always kept closed, except when charging. A series of these furnaces are built in a row and the products of combustion from each furnace containing the zinc oxide fume pass into common pipe lines to the collecting system. In operation a thin layer of anthracite coal, nut size, is placed on the grate,



FIG. 58. — STOCK TRESTLE. — PALMERTON WORKS.

and assisted by a light blast is allowed to burn until ignited. When burning in all parts, ore mixed with about half its weight of finely powdered anthracite coal and sometimes limestone, according to the composition of the ore, is spread in a layer five to seven inches thick over the ignited fuel and the doors at each end of the furnace closed, the blast being slowly admitted under the grate and increased to the maximum as required. During the charging, a damper in the pipe over the furnace is closed so that the gases produced cannot go to the bag-room. The zinc is reduced to the metallic condition, volatilized and, immediately catching fire, is burned to a dazzling white fume, which is drawn away by the suction fans.

217. At the end of about six hours the operation is complete, upwards of 90 per cent of the zinc in the ore having been driven off as the oxide, the remainder together with the iron and manganese being left in the residue on the grate. One man usually attends to a block of six double furnaces, charging them one after the other at intervals of one hour, which insures the necessary uniformity in the process. The ashes are removed from below the grate once in twenty-four hours. The charge of prepared ore for a double furnace is about five hundred pounds.

218. Collection of the Fume. The white fume escaping through the flue in the top of each furnace passes into a large common pipe line extending above the furnaces which leads to two brick towers where the heavier and less pure particles of oxide settle out. The somewhat purified fume is then blown by means of fans to a large cooling room where a further settling takes place. The fume, which is now quite cool, passes on to the bag-rooms, where the main pipes or flues are joined to several distributing sheet-iron pipes in the top of the bag-rooms. From each

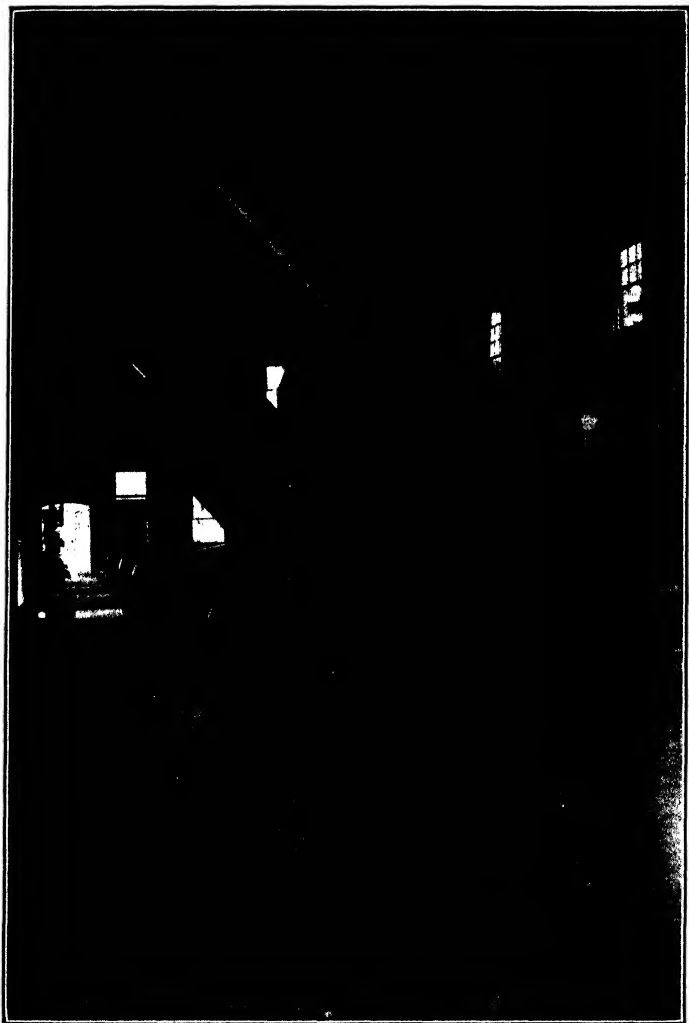


FIG. 59. — BLOWER ROOM. — PALMERTON WORKS.

pipe hang muslin bags 6 feet in diameter and about forty feet in length. The products of the combustion of the fuel contained in the fume pass through the bags, while the condensed oxide of zinc collects inside and is shaken down at regular intervals, a somewhat disagreeable task, as the atmosphere in the bag-room is strong with the escaping sulphurous acid gas. The zinc oxide after removal from the bags is graded according to color and purity and then bolted through silk cloth in machines similar to those used for bolting flour and packed into barrels holding about 200 pounds, in which form it is put on the market.

219. Palmerton Plant. The Palmerton plant of the New Jersey Zinc Company contains 24 blocks of oxide furnaces, 12 furnaces to the block, or a total of 288 furnaces, and as about 200 square feet of bag surface is required for 1 square foot of grate surface, this means about 850,000 square feet of bag surface, equal to 27 miles of bags, which are contained in four bag-rooms, having a combined floor area of nearly two acres. Eight exhaust fans, each driven by its own motor, are required for conveying the fume from the furnaces to the bag-houses. The bag-houses and packing house form a rectangle. The packing house is four stories in height, and the first and fourth floors contain enormous bins for the storage of unpacked oxide. By means of an electric elevator the oxide is sent to the bolting machines on the third floor, and then to the barrel packing machines on the second floor. The barreled oxide is then conveyed to the warehouses, which have a capacity of 9,000,000 pounds of oxide.

220. Purity of New Jersey Zinc Oxide. The Wetherill process, while simple in principle, is subject to the same difficulties that always attend a sublimation or volatilization process, as all of the volatile constituents of the ore as well as some of the constituents of the clinker ash pass over

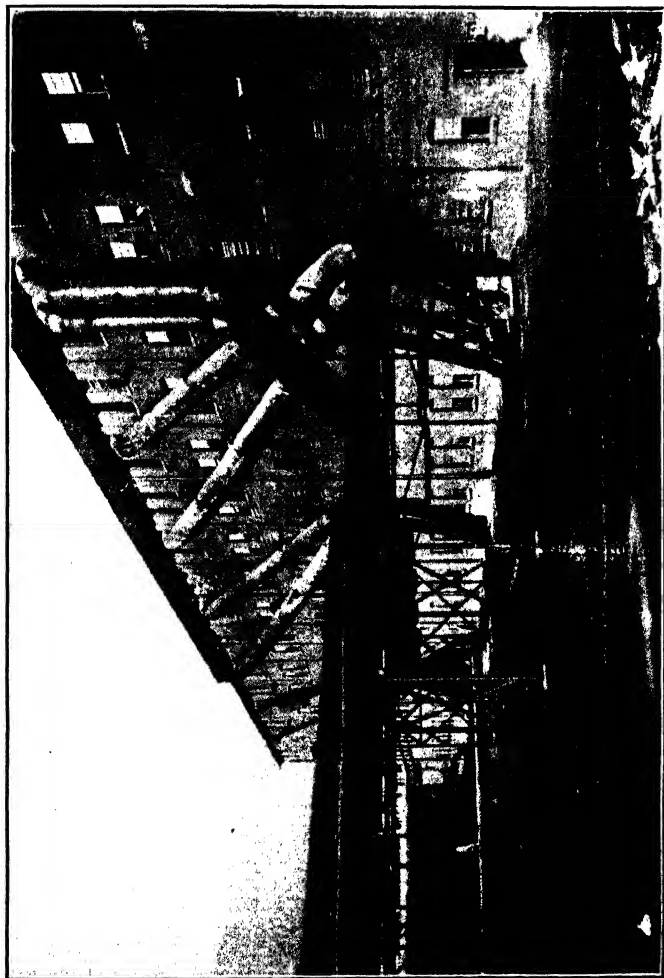


FIG. 60. — BAG-ROOM BUILDING. — PALMERTON WORKS.

and are collected with the oxide. This will include arsenic, antimony, cadmium, sulphur dioxide, lead, iron, manganese, silica, lime, and magnesia. The art of the manufacturer consists in keeping these impurities down to a negligible quantity. Under average conditions the purity of New Jersey zinc oxide is about as follows:

<i>Name.</i>	<i>Purity.</i>
"Special"	99.121 per cent.
"xx Red"	98.796 per cent.
"Selected"	99.227 per cent.
"xx"	99.051 per cent.

221. Zinc oxide produced from the metal itself as exemplified by the Florence Green Seal and Florence Red Seal brands contains 99.448 per cent and 99.336 per cent, respectively, of zinc oxide, which indicates that the production of oxide from the ore has reached an extremely high state of development and metallurgical perfection.

222. Furnace Assays. Variations in the character of the ore necessitate different conditions of heat, air and fuel supply, and a certain relation between the volume of the gas, the amount of zinc oxide that it carries and the dimensions of the flues and mains must be adhered to. According to Ingalls (*Metallurgy of Zinc and Cadmium*), the average furnace charge consists "of 100 parts of Franklinites, 55.68 parts of reducing coal and 49.95 parts of heating coal. The ore assaying about 34 per cent of zinc oxide yielded 24.50 per cent of first quality zinc oxide assaying 99.87 per cent zinc oxide, and 1.5 per cent of second quality assaying 99.34 per cent. The residuum amounted to 66.22 per cent of the ore. Its composition, according to C. F. McKenna, was about 36.43 per cent ferric oxide, 15.83 per cent manganese oxide, and 9.85 per cent zinc oxide, but the percentage of

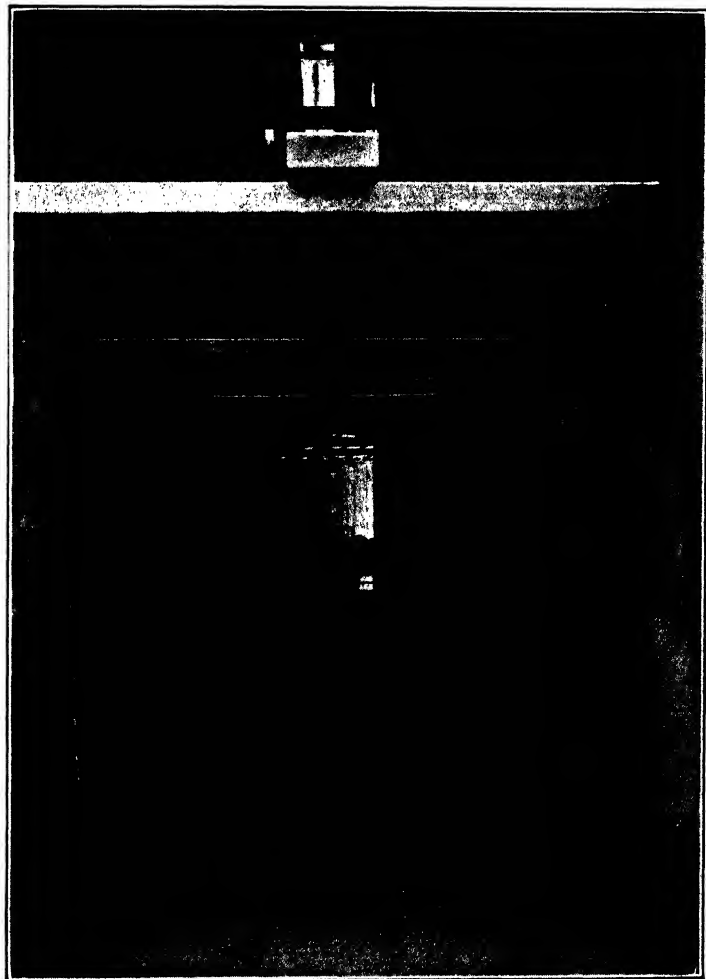


FIG. 61. — A BAG-ROOM. — PALMERTON WORKS.

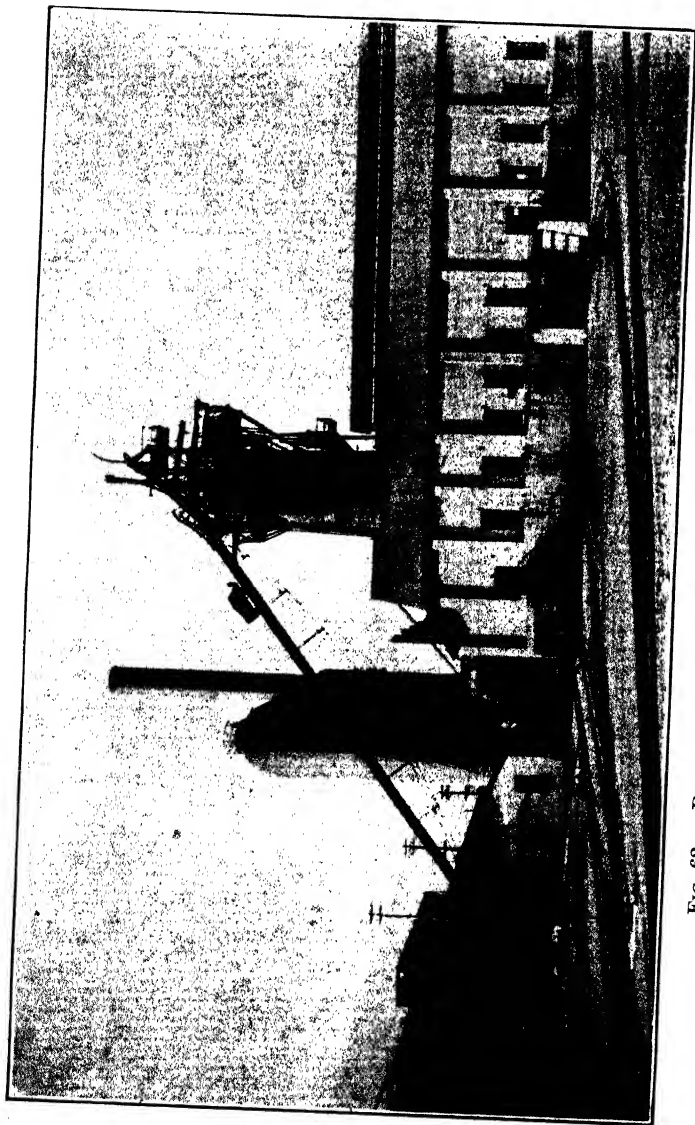


FIG. 62. — BLAST FURNACE FOR SPIEGELEISEN. — PALMERTON WORKS.

zinc oxide was sometimes as high as 11.85 per cent. Besides the iron, manganese and zinc oxides the residuum contains lime, magnesia, and alumina."

223. The ores at Franklin have proved to be particularly well adapted for producing oxide as they are practically free from the impurities which are most objectionable in the pigment, that is, lead, cadmium and sulphur.

However, since the introduction of magnetic separation the Franklinite ore used has averaged only about 28 per cent zinc oxide, of which about 83 per cent is volatilized and collected as zinc oxide.

224. Spiegeleisen. The residuum remaining in the oxide furnace is smelted in blast furnaces for spiegeleisen. In this process the zinc is reduced, volatilized and partially oxidized, and when obtained in the condensing system a portion of it is collected as a blue powder containing about 90 per cent zinc, and the remainder as a yellowish brown dust containing about 75 per cent of zinc oxide, and is sent to the spelter furnaces for reduction.

225. Mineral Point Works. At the Mineral Point works the zinc oxide is made by a process very similar to the above, the only difference being that there is a much more elaborate system of flues and dust-chambers between the furnaces and bag-rooms. The sulphur dioxide liberated from the ore is used for the manufacture of sulphuric acid. Very few of the Western ores are well adapted for the manufacture of oxide as they are generally less pure than the ore from Franklin, containing, especially, lead, so that the Western oxide always contains sulphate of lead. This varies in the different grades from a fraction of one per cent to nearly 25 per cent. Sulphate of lead is quite different from white lead, being a much more inert material, which is not so poisonous and not so likely to be discolored by the action of sulphur gases. In the West the same amount of

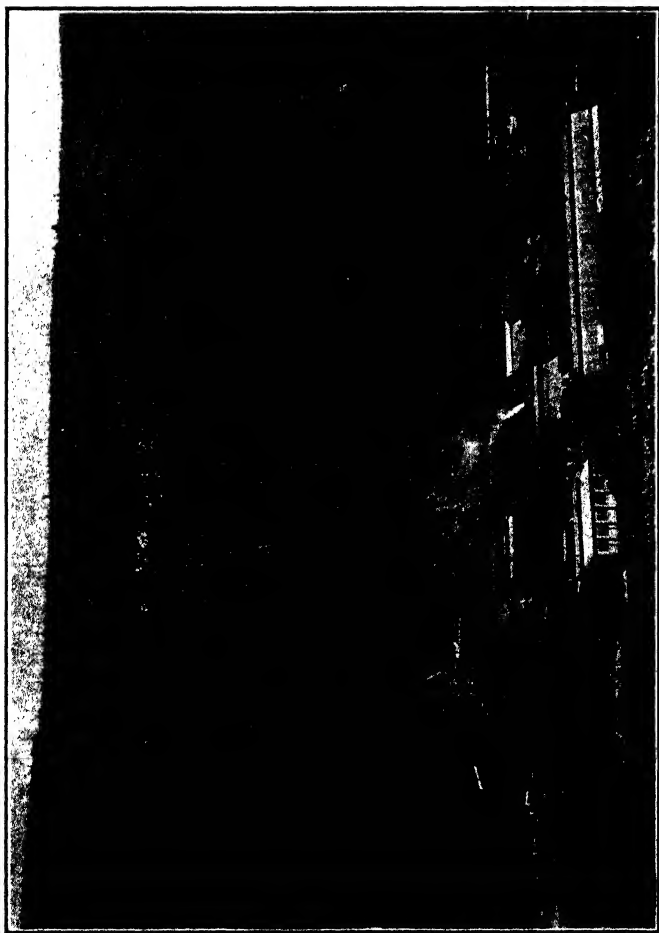


FIG. 63. — SPELTER PLANT. — PALMERTON WORKS.

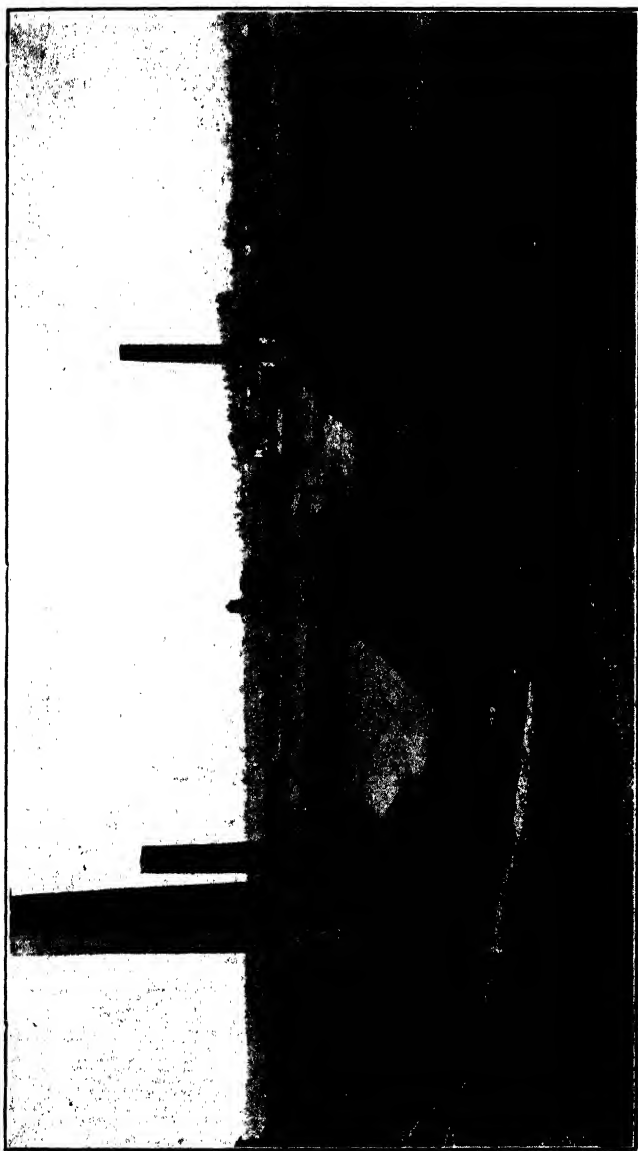


FIG. 64. — PLANT OF MINERAL POINT ZINC COMPANY.

care must be exercised as in the East, and in addition great skill is needed in mixing the various ores in proper proportions, so as to obtain a good quality of product. The grading in the East is almost entirely by color, but in the West, it is by both color and lead content.

CHAPTER XV.

PROPERTIES AND USES OF ZINC OXIDE.

226. Properties. Zinc oxide is perhaps the whitest of the valuable pigments at the disposal of the painter and paint manufacturer. It has a specific gravity of about 5.60 as compared with 6.45 for white lead, and is a much more voluminous or bulky pigment, a gallon measure containing only three to five pounds of loosely filled oxide. When hot it possesses a lemon yellow color, but on cooling regains its original whiteness. Heated by means of an oxyhydrogen flame, it emits a brilliant white light and after cooling, exhibits a marked phosphorescence in the dark, for a considerable length of time. In the electric furnace it rapidly volatilizes and condenses in long transparent crystals.

227. Solubility. Zinc oxide is readily soluble in all of the common acids, such as hydrochloric, sulphuric, nitric, and acetic acids, affording colorless solutions, and is not readily precipitated from them by alkalies, as zincates are formed which are quite soluble. One of the simplest tests for the presence of zinc in a pigment or paint is to dissolve a portion of the sample in hydrochloric acid, precipitate any iron and aluminum that may be present with ammonia, filter, make slightly acid with hydrochloric acid, and then add a few drops of potassium ferrocyanide. A gelatinous whitish precipitate indicates the presence of zinc.

228. Composition of Commercial Grades. Zinc oxide varies in purity according to the ore from which it is produced, and the method of furnacing. The following analyses drawn from various reliable sources will give some idea commercial grades to be found on the market.

229. Analyses of Oxide of Zinc made from the Ore.

	Eastern.			
	Special.	XX Red.	Selected.	XX.
	Per cent.	Per cent.	Per cent.	Per cent.
Insoluble.....	.045	.047	.025	.024
Water (H ₂ O).....	.302	.530	.230	.246
Carbonic acid (CO ₂).....	.019	.089	.019	.007
Sulphuric acid (SO ₃).....	.215	.261	.183	.249
(Total sulphur as)				
Sulphurous acid (SO ₂).....	.027	.057	.067	.046
(Red. Power equiv. to)				
Chlorine (Cl).....	.066	.078	.065	.074
Carbon (C).....				
Oxide of lead (PbO).....	.042	.031	.118	.171
Oxide of cadmium.....	Trace	Trace	Trace	Trace
Oxide of bismuth (Bi ₂ O ₃).....	None	None	None	None
Oxide of copper (CuO).....	None	None	None	None
Oxide of tin (SnO ₂).....				
Oxide of silver (Ag ₂ O).....				
Oxide of iron (Fe ₂ O ₃).....	.020	.011	.045	.092
Oxide of manganese (MnO).....	.017	.013	.017	.017
Alumina (Al ₂ O ₃).....	.022	.005		
Lime (CaO).....	.078	.054		
Magnesia (MgO).....				
Arsenious acid (As ₂ O ₃).....	.026	.028	.011	.023
Oxide of antimony (Sb ₂ O ₃).....	Trace	Trace	Trace	Trace
Oxide of zinc.....	99.121	98.796	99.227	99.051

230. Analyses of Zinc Oxide made from Spelter.

	Florence Green Seal.	Florence Red Seal.
	Per cent.	Per cent.
Insoluble.....	0.030	0.049
Water (H ₂ O).....	0.010	0.044
Carbonic acid (CO ₂).....	None	0.003
Sulphuric acid (SO ₃) (Total sulphur as).....	0.157	0.151
Sulphurous acid (SO ₂) (Red Power equiv. to).....	0.003	0.005
Chlorine (Cl).....	0.031	0.088
Carbon (C).....		
Oxide of lead (PbO).....	0.299	0.285
Oxide of cadmium.....	Trace	Trace
Oxide of bismuth (Bi ₂ O ₃).....	None	None
Oxide of copper (CuO).....	None	None
Oxide of tin (SnO ₂).....		
Oxide of silver (Ag ₂ O).....		
Oxide of iron (Fe ₂ O ₃).....	0.022	0.039
Oxide of manganese (MnO).....	Trace	Trace
Alumina (Al ₂ O ₃).....		
Lime (CaO).....		
Magnesia (MgO).....		
Arsenious acid (As ₂ O ₃).....	Trace	Trace
Oxide of antimony (Sb ₂ O ₃).....	Trace	Trace
Oxide of zinc (ZnO).....	99.448	99.336

231. Analyses of Mineral Point Zinc Oxides.

	Prime.	Standard.	Sterling.	Leaded.
Insoluble.....	0.04	Trace	0.09	Trace
Water (H ₂ O).....	0.06	0.90	0.11	0.11
Carbonic acid (CO ₂).....	0.10	0.08	0.08	Trace
Sulphuric acid (SO ₃) (Total sulphur as).....	1.25	1.63	3.42	5.62
Sulphurous Acid (SO ₂) (Red. Power equiv. to).....	0.033	0.05	0.03	0.08
Chlorine (Cl).....	0.05	N D	N D	N D
Carbon (C).....	None	N D	N D	N D
Oxide of lead (PbO).....	2.72	3.80	8.79	15.08
Oxide of cadmium (CdO)....	0.06	0.14	0.25	0.17
Oxide of bismuth (Bi ₂ O ₃)....	None	N D	N D	N D
Oxide of copper.....	None	N D	N D	N D
Oxide of tin (SnO ₂).....	None	N D	N D	N D
Oxide of silver (Ag ₂ O).....	None	N D	N D	N D
Oxide of iron (Fe ₂ O ₃).....				
Alumina (Al ₂ O ₃).....	0.08	0.05	0.06	0.05
Lime (CaO).....	None	Trace	N D	N D
Magnesia (MgO).....	None	Trace	N D	N D
Arsenious acid (As ₂ O ₃).....	0.12	N D	N D	N D
Oxide of antimony (Sb ₂ O ₃)....	None	N D	N D	N D
Oxide of zinc (by difference).	95.52	93.40	87.39	78.97
Equivalent to				
PbSO ₄	3.70	5.17	11.95	20.50
ZnSO ₄	0.42	0.40	0.45	0.24
PbSO ₄ range.....	0 to 5.00	0 to 5.00	5.00 to 16.00	16.00 to 25.00

232. Analyses of Zinc Oxide.¹ — Scott.

	I	II	III	IV	V
Zinc oxide.....	99.80	96.81	89.31	77.35	48.40
Zinc sulphate.....	0.00	0.15	0.96	0.13	0.67
Lead sulphate.....	0.00	2.75	9.33	21.01	50.40
Lead oxide.....	0.00	0.00	0.27	1.38	0.32
Insoluble matter.....	Trace	0.22	0.03	0.08	0.10
Moisture.....	0.20	0.07	0.10	0.05	0.11
Specific gravity.....	5.560	5.795	5.620	5.800	5.770

- I. Pure zinc oxide made from spelter.
- II. Zinc oxide made from silicate ore.
- III. Zinc oxide made from blende.
- IV. Leaded zinc oxide made from mixed ore.
- V. Zinc-lead made from zinc and lead ores.

¹ Scott, Oxide of Zinc, page 15.

233. Hooker in his pamphlet on "Zinc White" records the following analyses:

	I	II	III	IV	V
Zinc oxide.....	98.80	98.40	93.60	92.90	84.60
Sulphur dioxide.....	0.007	0.04	0.08	0.43	0.06
Zinc sulphate.....	0.35	0.89	1.29	4.35	1.16
Lead sulphate.....	0.35	0.00	4.60	1.60	13.63
Moisture.....	0.24	0.30	0.20	0.31	0.21
	99.747	99.63	99.77	99.59	99.65

234. **Sulphur Dioxide and Zinc Sulphate.** Variation in the lead content of a commercial zinc oxide is of small moment, as compared with the percentages of sulphur dioxide and zinc sulphate, and as Hooker states, if these impurities are not largely eliminated, "the grinder's troubles are many and livering and granulation of the paint can be looked for."

235. **Imported Zinc Oxides.** The imported zinc oxides are prepared, as has been explained, from the burning of the metal or spelter; they possess exceeding whiteness and when used with tinting colors exhibit a purity of tone far surpassing white lead, as can be easily demonstrated by preparing two light blues of as nearly the same tint as possible, using in the one case Prussian blue and zinc oxide and in the other case white lead and Prussian blue; it will be found that the blue prepared with the zinc oxide is of a very much cleaner tint. Using equal quantities of Prussian blue it will be noticed that only about one-half as much zinc oxide is required to produce substantially the same tint as with white lead (Old Dutch process). Stated in more accurate terms the tinting strength of zinc and lead, weight by weight, is as 11 is to 20.

236. Comparative Prices. The domestic Florence Green Seal and Red Seal oxides prepared from the metal are substantially equal to the imported oxides, and in the opinion of the writer may be substituted with advantage in almost every instance for them. The following figures (1908) show the comparative prices of the various zinc oxides:

Paris Green Seal	10 $\frac{3}{4}$ cents f.o.b. New York.
Paris Red Seal	8 $\frac{3}{4}$ cents f.o.b. New York.
Antwerp Green Seal	10 $\frac{1}{2}$ cents f.o.b. New York.
Antwerp Red Seal	8 $\frac{1}{4}$ cents f.o.b. New York.
Florence Green Seal	7 cents f.o.b. Philadelphia.
Florence Red Seal	6 $\frac{1}{2}$ cents f.o.b. Philadelphia.
New Jersey XX	5 cents f.o.b. Detroit.
Zinc Lead White	4 $\frac{1}{2}$ cents f.o.b. Detroit.

237. Lack of Affinity for Moisture. One of the greatest faults to be found with the zinc oxide pigments is their lack of affinity for damp surface, i.e., paints high in zinc oxide lack penetration when applied over a damp surface, the resulting manifestations being peeling and cracking. It is the custom with many painters to cover kegs of strictly pure white lead with a little water to prevent the formation of "skins." In the case of combination white leads containing zinc oxide, such treatment is detrimental, as it usually results in the hardening of the lead and the formation of "crusts."

238. Zinc Oxide as a Paint Pigment. Much has been written about the properties of zinc oxide and its value as a paint pigment. Judging from the experience of American paint manufacturers it has not proved satisfactory when used alone as a pigment for outside house paints owing to its excessive oil-taking capacity, producing a very thin coat and the production of a hard brittle paint film. As a base for enamels, however, it leaves but little

to be desired as regards whiteness, body and wearing value. By far the larger amount of zinc oxide produced is used in the manufacture of mixed paints and combination white leads. When used with lead pigments maximum wearing value is undoubtedly secured, although paint manufacturers are not agreed as to the most desirable proportions. Climate and locality have much to do with this lack of agreement.

239. Along the sea coast a paint high in lead and low in zinc has not proved satisfactory, and the writer is informed that the best lighthouse specifications call for 75 per cent zinc and 25 per cent lead. Inland, the same conditions do not hold, and in the majority of high class paints the zinc and lead pigments are present in not far from equal quantities, disregarding any inert pigments that may be present. Sixty-one analyses, made by the writer, of the leading brands of mixed paints sold in this country, showed an average ratio of lead pigments to zinc oxide of 45:55. Paints prepared expressly for inside use are usually high in zinc and low in lead, the ratio being usually 75-80 parts zinc to 25-20 parts lead. This is due primarily to the fact that zinc oxide is not affected by sulphur gases in the same way as white lead, as zinc sulphide is white whereas lead sulphide is black, and therefore, a paint containing a large quantity of white lead used on interior work will soon darken, especially where gas or coal is burned. The inertness of zinc oxide toward the various tinting colors also renders it especially valuable in the manufacture of tinted mixed paints, notably the blues, yellows and greens.

240. The foregoing statements will give some idea of the uses and extent to which zinc oxide has been put in the paint industry as compared with white lead. A glance at the following table of production shows that the use of

zinc oxide as a pigment is rapidly on the increase. This is true not only in the regular lines of house paints but in the special lines as well, such as dipping paints and enamels, as a base for striking organic colors upon, etc. When it is considered that zinc oxide is a very young pigment as compared with white lead, it having been in use for only a comparatively short period of years, it is evident from the ready favor with which it has been received by paint manufacturers as indicated by its present enormous consumption that it at least merits equal importance and consideration with white lead.

241. Production and Value of Zinc Oxide, 1880-1907.

Year.	Quantity.	Value.	Year.	Quantity.	Value.
1880	20,214,000	\$763,738	1894	39,974,000	\$1,399,090
1881	20,000,000	700,000	1895	41,420,000	1,449,700
1882	20,000,000	700,000	1896	40,000,000	1,400,000
1883	24,000,000	840,000	1897	50,000,000	1,750,000
1884	26,000,000	910,000	1898	66,000,000	2,310,000
1885	30,000,000	1,050,000	1899	80,292,000	3,211,680
1886	36,000,000	1,440,000	1900	97,680,000	3,667,210
1887	36,000,000	1,440,000	1901	93,000,000	3,720,000
1888	40,000,000	1,357,600	1902	105,460,000	4,023,299
1889	33,940,000	1,357,600	1903	125,924,000	4,801,718
1890	1,600,000	1904	126,626,000	4,808,482
1891	47,400,000	1,600,000	1905	136,206,000	5,520,240
1892	55,000,000	2,200,000	1906	159,360,000	5,999,375
1893	48,118,000	1,804,420	1907	143,568,000	6,490,660

CHAPTER XVI.

MANUFACTURE OF LEADED ZINCS.

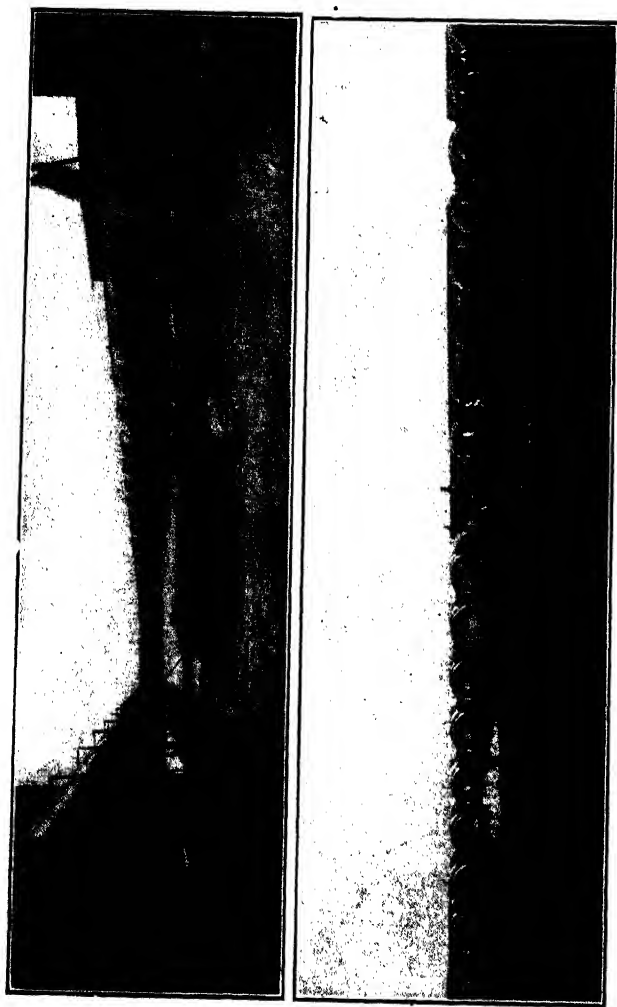
242. History. The success of the Eastern manufacturers in the manufacture of zinc led Western metallurgists to believe that a zinc oxide pigment could be prepared from the complex Ozark zinc ores, which are essentially the sulphide, carbonates and silicates of zinc and lead. A company was formed for this purpose in 1900, and a plant with four furnaces constructed at West Plains, Mo., which shortly afterwards, however, proved too weak financially to make the experiments and improvements necessary for the perfecting of the process. With the data acquired by this attempt a new company was organized at St. Louis, and works built near Joplin, Mo., which after numerous attempts succeeded in preparing a fairly satisfactory pigment. The success of the project being evident, another plant was constructed at Coffeyville, Kan., which began operations in April, 1906. The erection of the second block of furnaces and bag-room was completed in the summer of 1907, the plant now having a capacity of about sixty tons of ore daily.

243. Comparison with Eastern Methods. The methods used in these plants differ considerably in details from those in use in the Eastern oxide plants, from the fact that the Eastern ores are substantially free from lead, while the Western ores contain varying amounts, ranging from three to twenty per cent. Also anthracite coal or coke is used for the furnace fuel in the East, while soft or semi-anthracite coal is almost entirely used for the manufacture of Western

zinc oxides. The hydrocarbons produced by the use of soft coal made it necessary to change much of the anthracite process in order to secure complete combustion so that the zinc oxide would not be discolored.

244. Process of Manufacture. All grades of ore may be used, from zinc ores containing no lead up to ores containing equal amounts of lead and zinc, the only requirements being that the combined assay of lead and zinc does not fall below 30 per cent, as ores having less than 30 per cent are not profitable to work in the furnace. Usually the ores can be concentrated so as to bring the average up to this figure, or high grade ore can be added until the content is raised to the desired point. As obtained in actual practice the ratio of zinc to lead in the mixed ore is about two to one.

245. The mixed ores are sized and roasted in McDougall furnaces to a proper sulphur content, the amount of sulphur left in the ore depending on the amount required to combine with the lead to form sulphate of lead. The roasted ore is then taken to the pigment furnaces, of which there are 2 blocks of 18 furnaces each, at the Coffeyville works, the size of the individual furnaces being 6 feet by 12 feet. The grates are perforated in the usual manner, i.e., with conical holes, having a diameter of one-eighth inch at the top, the holes being one and one-half inches apart. The furnaces are charged with a thin layer of semi-anthracite coal, common to that section of the country, and when this is burning freely, the mixed charge of ore and coal is distributed evenly over the grate. The zinc oxide and lead sulphate pass off as a fume, under carefully regulated conditions, through several hundred feet of cooling pipe, which makes a large horse-shoe turn, as illustrated, conveying the fume to the bag-room, where it is collected in muslin bags in much the same manner as in the Eastern plants. This process requires about one hundred and fifty square



**UPPER CUT. — FIG. 65. — PIPE LINE. — COFFEYVILLE PLANT (Courtesy of the Eng. and Mining Journal).
LOWER CUT. — FIG. 66. — FURNACES IN COURSE OF CONSTRUCTION. — COFFEYVILLE PLANT (Courtesy of
the Engineering and Mining Journal).**

feet of muslin in the bag-room for every square foot of grate surface in the pigment furnaces. The coarser particles of the sublimate are deposited in the cooling pipe, which is provided with cleanout doors at regular intervals, as shown in the illustration.

246. Characteristics. The samples of oxide produced by this process that have been examined by the writer were not as white as the New Jersey oxides, and are liable to contain considerable amounts of zinc sulphate and sulphur dioxide, the bad effects of which are well known to the paint trade, and have been discussed to some extent in other portions of this book. The following analyses, made at different times by the author, are believed to be representative of zinc-lead pigments of this type, although the source of these samples was not known to an absolute certainty.

	I.	II.	III.
	Per cent.	Per cent.	Per cent.
Moisture.....	0.03	0.02	0.04
Sulphur dioxide.....	0.30	0.29	0.50
Zinc sulphate.....	0.86	1.49	1.26
Lead sulphate.....	26.46	19.76	23.06
Zinc oxide.....	72.11	78.11	74.72
Undetermined.....	0.24	0.33	0.42
	100.00	100.00	100.00

247. The above figures indicate that the furnace charges were not prepared as carefully with regard to the lead and zinc content as would have been expected. In the recent analyses made by the writer on "zinc lead white" the writer has seldom found the lead or zinc content to vary more than three per cent. As several of the leading paint chemists reject zinc pigments containing more than 0.06 per cent of sulphur dioxide and zinc sulphate in excess of one per cent it is probable that pigments typical of the above analyses would be rejected as constituents of high class paints.

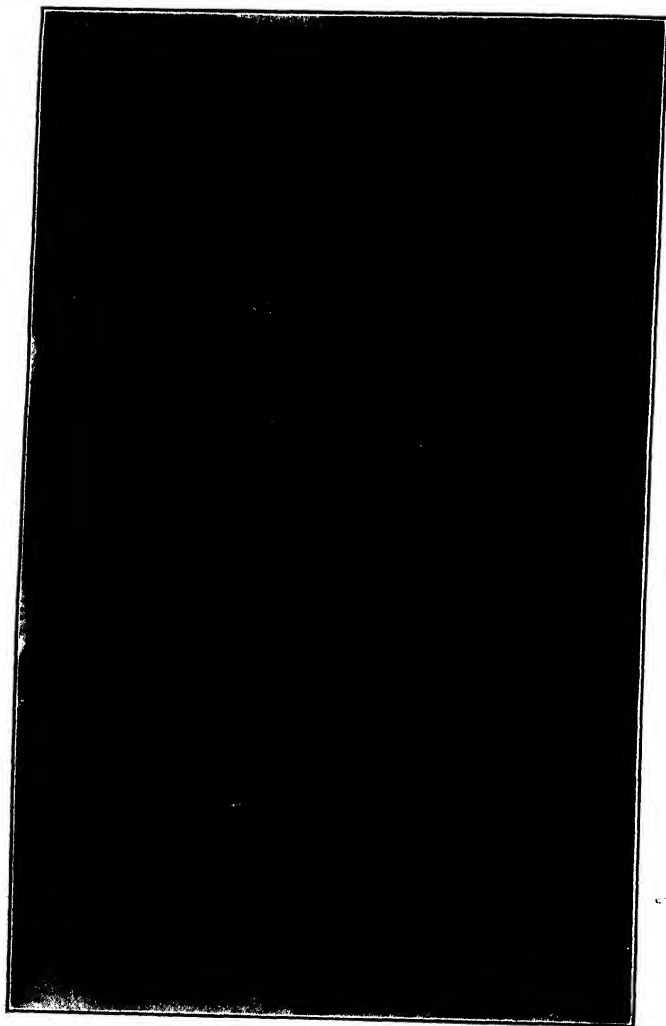


Fig. 67.—FORMATION OF ZINC SULPHATE ON PAINT FILM.

248. Zinc Sulphate. The preceding illustration, Fig. 67, which is from a photograph taken by the writer, shows the effect of zinc sulphate when in appreciable quantity. This test was three coat work over new pine clapboards. The paint employed was of a lead color, the white base of which contained white lead, zinc oxide, barytes and a leaded zinc containing an excess of zinc sulphate. The test had been under inspection for nine months, when the phenomenon illustrated manifested itself. A number of heavy dews preceded by a long spell of dry hot weather caused the formation of numerous drops of moisture on the lower portions of the clapboards each night, which evaporated during the following day. These drops of moisture soaked and penetrated the paint film thoroughly, and brought to the surface and left on evaporation a white deposit. A chemical examination showed that this white substance was a nearly pure sulphate of zinc which was not as readily soluble in water as normal zinc sulphate, and by further tests was proved to be a basic sulphate.

249. Result on Life of the Paint. The extent of the deposit is evident from the photographic illustration. A paint composed of the pigments enumerated above would not have saponified the oil sufficiently in nine months to render the film sufficiently porous for the ready lixiviation of sparingly soluble salts unless there was present an astringent, as it were, which had destroyed the vitality or life of the oil. There was nothing in the nature of the drier or in the quantity used that might be expected to cause such a result, especially when it is noted that the white lead constituted less than 20 per cent of the pigment. It is evident that a paint film in which the oil has lost its vitality cannot be expected to give a satisfactory wearing value, which was amply shown to be the case in this instance by the subsequent inspections.

CHAPTER XVII.

ZINC LEAD WHITE.

250. Source. The larger portion of the lead and copper ores obtained in the Western part of the United States contains varying quantities of the precious metals, gold and silver. The smelting and recovery of these four metals by well-known metallurgical processes is a simple matter as long as the ores do not carry appreciable quantities of zinc. In a large portion of these ores, however, zinc is present in considerable amounts and constitutes one of the greatest drawbacks to ordinary smelting methods. The reason for this is that no smelting method has yet been devised whereby zinc can be satisfactorily reduced and collected simultaneously with either lead or copper.

251. In the ordinary methods of smelting any zinc present in the ores is entirely lost by volatilization. This loss, while serious, is not of so much importance as the difficulty encountered in freeing the ore from it. As is well known, all the substances entering into a smelting furnace charge must be reduced and collected in metallic form, melted to a fluid slag which goes to waste, or burned to gases which escape, as is the case with the coke. Zinc is extremely volatile at the comparatively high temperature necessary for ordinary furnace operations, and if the zinc is allowed to volatilize and escape in this manner, the losses of gold and silver are such as to render the process unprofitable. Hence the only course left is to convert the zinc into the oxide and then have it taken up by the slag, which is often a very unsatisfactory solution of the problem, as the zinc is taken

up only with difficulty, resulting in the lengthening of the furnace operations and in considerable increased cost of slag material and fuel. It also causes a serious loss of other metals present, as a zinc slag is not as clean as one without zinc.

252. Early Manufacture. The facts above cited rendered it impossible to treat the low grade complex gold ores, which are obtainable in enormous quantity in the Rocky Mountain region, by the ordinary methods of smelting. The obvious solution of the problem was the successful removal of the zinc. This was accomplished by the American Zinc Lead Company, who constructed a small plant in Canon City, Colorado, commencing operations in the spring of 1891. The metallurgical methods used in this plant were in many ways the reverse of ordinary methods, the zinc and lead being removed as the first step by volatilization as a "fume" which was collected and put on the market as paint pigment under the name of zinc lead white. This process left the copper, gold and silver in the furnace cinder, which was then smelted out in the regular way.

253. Absorption by United States Smelting Company. At the inception of the industry, the pigment obtained, i.e., the zinc lead white, was considered as a by-product and of minor importance, the profitable recovery of the copper, gold and silver being the main object; consequently little regard was paid to the varying proportions of the volatile constituents — zinc and lead — and hence the pigment varied constantly in composition and color. In 1902, the plant process and patents were taken over by the United States Smelting Company and the plant enlarged greatly.

254. Standard of Composition. In order to obviate variations in composition as far as possible, a standard of

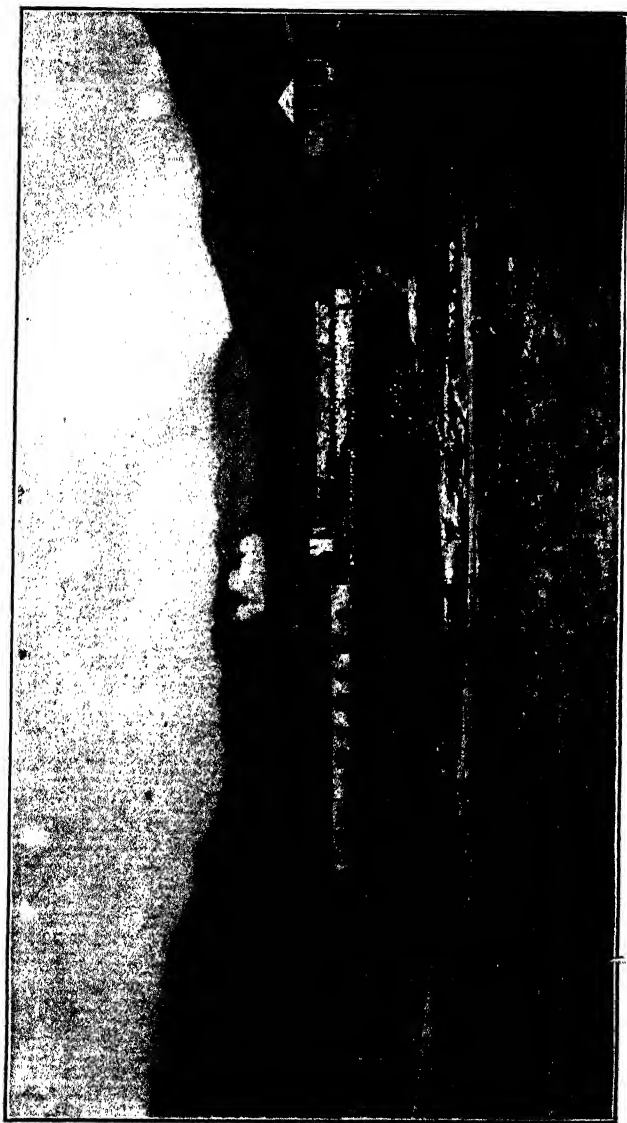


Fig. 68. — ZINC LEAD PLANT. — U. S. SMELTING COMPANY.

proportional contents of lead and zinc was adopted for the pigment and the charges of ore were prepared for furnacing on the basis of chemical analysis, resulting in the production of a pigment which runs approximately fifty per cent zinc oxide and fifty per cent lead sulphate. The ores and concentrates operated on, while low in gold and silver, are high in the zinc and lead content, even higher than the average lead and zinc ores.

255. Sublimation of Fume. The ore on receipt at the works is crushed and screened by suitable machinery and mixed in such proportions as will yield the desired ratio of zinc and lead in the finished pigment. The ore is then fed, together with a sufficient amount of fine coal or coke, into the volatilizing and oxidizing furnaces, which are so constructed as to admit air to the incandescent mass of ore and fuel on the grates, in proper supply and from all sides. The zinc and lead present is reduced to the metallic state, and instantly vaporized and drawn by the exhaust fans into combustion chambers where oxidation takes place, the zinc being converted into zinc oxide and the lead to lead sulphate.

256. Collection of Fume. These two products, being formed from a homogeneous gas into minute solid particles, are most closely associated together, existing in almost as close a union as though chemically combined. By reason of the suction fans, these minute particles, in the form of a white fume, are carried along through a series of cooling flues to suspended woolen collecting bags through which the sulphurous gases of the combustion pass, while the pigment is retained.

257. Final Treatment. The white pigment as it collects in quantity is removed from these bags and carried to the finishing furnaces where on open hearths, charged and discharged continuously, the crude product is further oxidized,

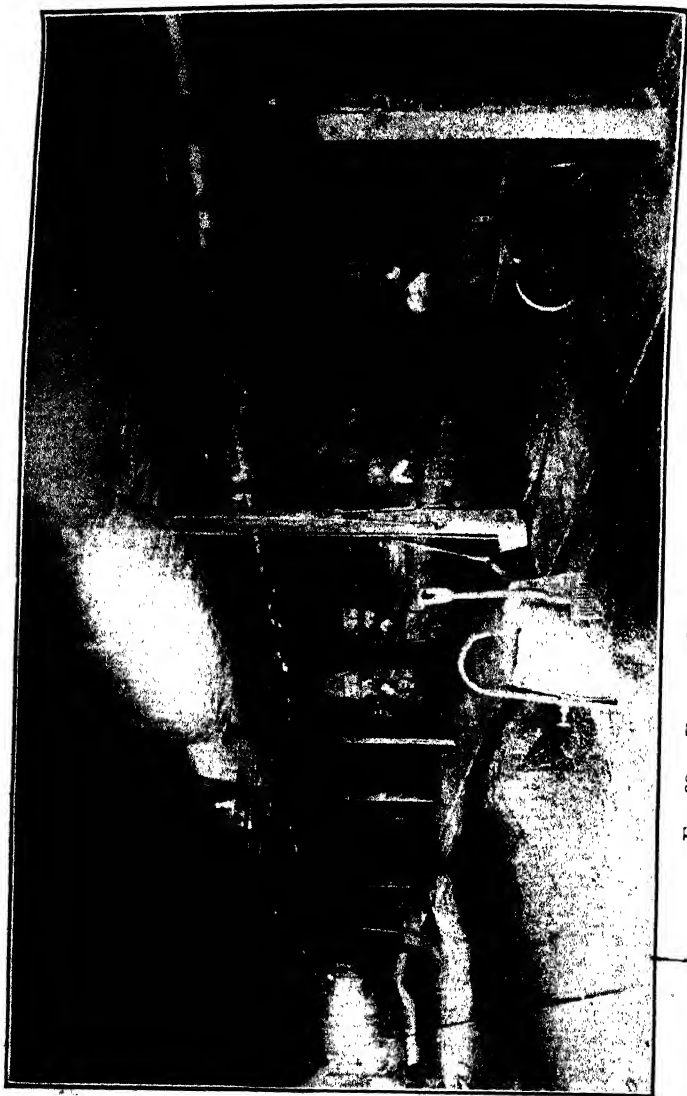


FIG. 69. — FURNACE ROOM. — U. S. SMELTING COMPANY.

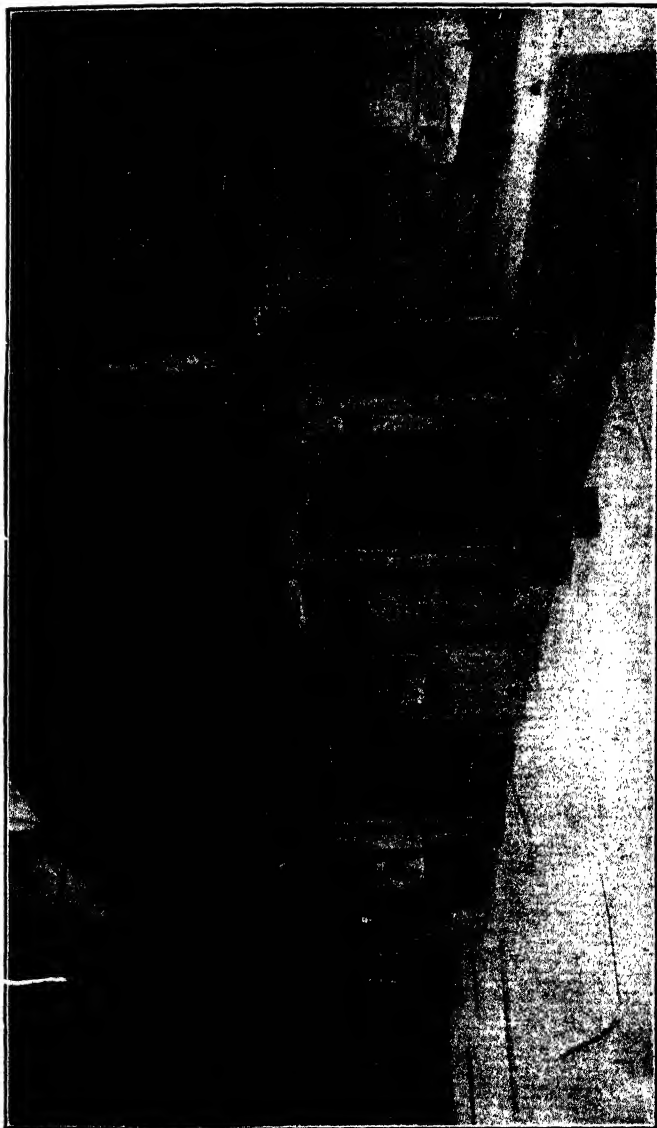


FIG. 70. — REFINING FURNACES. — U. S. SMELTING COMPANY.

condensed in bulk, desulphurized and whitened. Finally, the finished product is bolted through a fine cloth screen and packed for shipment.

258. Production. In 1892, about 24,000,000 pounds of low grade sulphide ore were treated by this process, producing 2,500,000 pounds of zinc lead white, 360,000 pounds of copper, 137,000 ounces of silver and 120 ounces of gold. The production of zinc lead white increased slowly until 1901, from which date the amount produced increased rapidly, as is shown in the following table —

ZINC LEAD WHITE.

Year.	Production in pounds.	Value.	
		Total.	Per lb.
1901	5,000,000	\$150,000	\$0.0300
1902	8,000,000	225,000	0.0281
1903	9,000,000	247,500	0.0265
1904	11,558,000	404,530	0.0350
1905	13,558,000	474,530	0.0350
1906	16,148,000	681,292
1907	27,032,000	1,286,440

259. Physical Properties. As produced, zinc lead white is intermediate in its properties between the lead and zinc pigments, resembling zinc oxide perhaps more than lead pigments, for instance, sublimed white lead, which is prepared much in the same way. The combination between the zinc oxide and the lead sulphate is probably not chemical in its nature, but may be described as an alloy of the two pigments, the temperature of production being exceedingly high, and therefore it is to be expected that the pigment would possess the individual characteristics of its components.



FIG. 71. — BAG-ROOM, — U. S. SMELTING COMPANY.

260. Recent Improvements. During the last few years there has been a marked improvement in its whiteness and uniformity of composition. The slight yellowish-gray tint that it possesses does not at all interfere with its use in ready mixed paints or combination leads. The very reasonable price at which this pigment has been offered to the trade has caused its rapid adoption by the paint manufacturers, and there are probably very few paint houses who do not find a use for it in some of their products.

261. Use in House Paints. Owing to the uniform fineness of the pigment particles of zinc lead white it produces a paint that brushes easily and flows out evenly, being one of the most satisfactory pigments we have in these respects. As a white base in conjunction with a small percentage of white lead and 25 to 40 per cent of zinc oxide, for tinted house paints zinc lead white has found a wide use. White lead, i.e., basic carbonate of lead, owing to its lack of chemical stability, is particularly unsuited for the production of tints containing chrome yellow, Prussian blue, chrome green and ultramarine blue owing to chemical interaction of these colors with the white lead causing a fading or darkening of the paint film as the case may be. The sulphates of lead, including the basic lead sulphate produced by the Picher Lead Company, have a much more stable constitution and are not easily affected by the tinting colors with which they may be used, and this, to the paint manufacturer, is a very serious consideration.

262. Use in the Manufacturing Trades. Zinc lead white finds perhaps its greatest use in paints for the manufacturing trades such as paints for farm implements, farm machinery, etc., especially where dipping is resorted to, i.e., the articles to be painted are dipped in large tanks of the prepared paint and the surplus paint allowed to drain off. In order for this operation to be uniformly

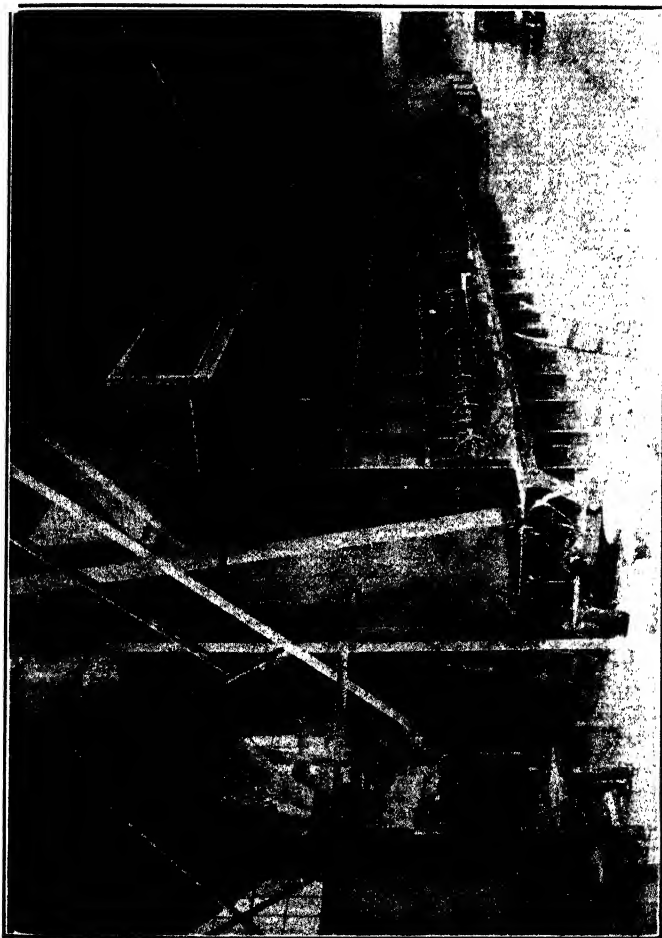


FIG. 72. — BARREL PACKER AND MIXERS. — U. S. SMELTING COMPANY.

successful it is necessary to use pigments which in addition to possessing the requisite body or hiding power must be non-settling in the rather thin vehicle employed. Zinc lead white meets these combined requirements excellently and is therefore almost universally used for this line of paints.

263. There has been some complaint in the past regarding the amount of arsenic present as an impurity in zinc lead white; at the present time, however, the arsenic can be considered as a negligible factor as it is usually less than 0.20 per cent, while New Jersey zinc oxide often contains 0.08 per cent and is used in far greater quantities and in higher percentages for interior work than zinc lead white.

264. Chemical Composition. There has been more or less claim that the lead in zinc lead white is in the form of an oxysulphate, but a careful comparison of the combined sulphuric acid with the amount of lead does not justify this view. Naturally under certain furnace conditions a small amount of oxysulphate may be formed, but the writer has never been able to find more than a fraction of one per cent. Being the product of a complex metallurgical operation it is to be expected that zinc lead white will vary slightly in composition even though the furnace charge is prepared on the basis of a chemical analysis so as to yield a pigment half lead sulphate and half zinc oxide. As above mentioned zinc sulphate is the leading impurity and owing to the nature of the process will always be present in a greater or less quantity, but with care can be kept to below one per cent, which is the limit set by several leading paint chemists. Considering the price at which this pigment is offered for sale it is one of the most acceptable paint pigments at the command of the paint manufacturer.

265. Zinc Sulphate. Used in outside house paints zinc lead white has caused some complaint due to the "washing"

of the paint film, a condition better observed than described, seeming to consist in the washing away of the pigment particles from the binder, causing either a streaked or faded appearance of the paint film. This effect is apparently due to the presence of zinc sulphate in the pigment, although the exact manner in which the action takes place is not clear. Some paint chemists have claimed that it was due to the astringent action of sulphur dioxide on the linseed oil, but as a matter of fact zinc lead white contains less than 0.01 per cent of sulphur dioxide, being purer in this respect than the New Jersey zinc oxides. In an extensive practical test conducted by the writer at the North Dakota Experiment Station, three ready mixed paints were applied, one of which was composed of straight zinc lead white; the second contained about 50 per cent of a leaded zinc from a different source, which in addition to zinc sulphate contained a considerable amount of sulphur dioxide; the third contained about forty per cent of zinc lead white. All three paints washed noticeably inside the first twelve months exposure, but the second paint, containing the sulphur dioxide, did not wash to any greater extent than did paint number three. The straight zinc lead white "washed" the most seriously of all, which indicated that the presence of other pigments restrained the "washing" to some extent.

266. This "washing," however, does not seem to be accompanied by any marked cracking, peeling, or chalking, providing the paint has been suitably applied, and such paint usually wears down to a uniform surface excellent for repainting.

CHAPTER XVIII.

THE OXIDES OF LEAD.

267. Classification. Lead forms five compounds with oxygen, as follows:

- Pb₂O, lead suboxide,
- PbO, lead monoxide,
- PbO₂, lead dioxide,
- Pb₂O₃, lead sesquioxide, and
- Pb₃O₄, red lead, orange mineral.

268. Not all of these forms find commercial uses, however, notably the suboxide and sesquioxide. The dioxide is used only to a limited extent, chiefly for electrical purposes. The monoxide, known under the two varieties, litharge and massicot, is produced in large quantities. The other oxide, which corresponds quite closely to the empirical formula Pb₃O₄, is also placed on the market in two modifications—red lead, sometimes known as minium, and orange mineral. Regarding the relation existing between red lead and the other oxides of lead nothing definite can be stated. Numerous chemists regard it as a mixture of the monoxide and dioxide (2 PbO + PbO₂), but perhaps the majority of authorities consider that the evidence leads to the conclusion that it is a chemical compound and not a mixture.

269. Lead Suboxide. This compound is formed when lead is exposed to air under certain conditions as when lead is atomized with a jet of steam as carried out in both the Carter and Mild process, the little particles of lead being

covered with a coating of the suboxide. As prepared it is black, but in moist condition is very susceptible to further oxidation.

270. Litharge (lead monoxide). The transformation of lead into a dry powder which we know as litharge, by exposing it to the action of heat, was known to the ancients, and was without doubt the first of the lead compounds known



FIG. 73. — OXIDE WORKS. — MATHESON & COMPANY.

to them, and Napier states that it has been found in the analyses made of the paints and glazes used by the ancient Egyptians for decorating their pottery. Maigue, in his *Dictionnaire Classique*, states that the art of making litharge originated in the East, and is supposed to have been known in the time of Solomon. Bricks and various articles of pottery which have been found in the ruins of Nineveh and Babylon are believed to have been glazed by the use of litharge.

271. Early Confusion regarding Nature of Litharge. As litharge occurs in several modifications, some of them granular and some flaky, varying in color from a light golden yellow to a buff color, it is not to be wondered at that the ancient writers were much confused in their descriptions of the product and the process of manufacture. Pliny apparently had some definite knowledge of this product, which he discusses under the name of "molybdena," stating, "It is considered better in quality, the nearer it approaches golden in color, and the less lead it contains (probably referring to metallic particles); it is also friable and of moderate weight; it is found adhering to furnaces in which gold and silver have been smelted." Later Dioscorides in discussing products made from lead states that a more difficult way of producing litharge is "burning the lead without admixture of any other substance." This is undoubtedly the earliest reference to the production of litharge from lead as a primary product.

272. Development of Litharge Industry. The use of litharge did not develop rapidly and it remained an article of comparative unimportance for a great many centuries. In the manuscripts of the Middle Ages it is mentioned rarely, and probably did not begin to find favor until about the fifteenth century. With the development of the white lead industry by the Dutch, it is only natural they should have attempted the manufacture of litharge and red lead on a comparatively large scale, but as far as litharge was concerned they did not meet with any great financial success, owing to their disadvantageous location, having to import their lead from countries where litharge was produced as a by-product, as in the seventeenth century we find the English exporting litharge in large quantities to all parts of Europe, it being obtained by them in refining of their argentiferous ores.

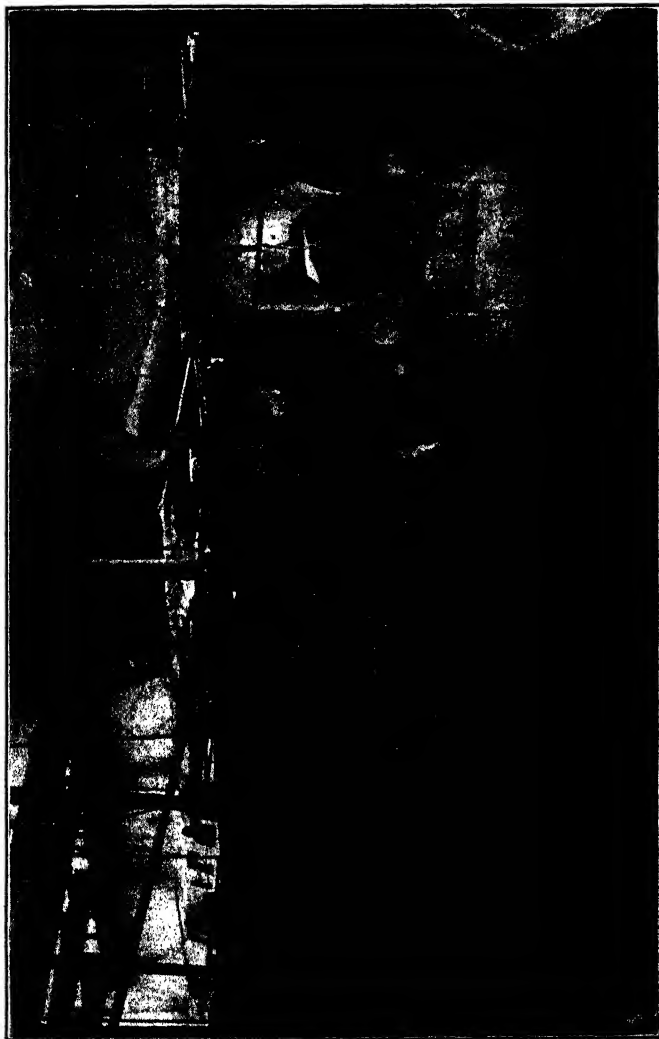


FIG. 74. — OXIDE FURNACES. — NATIONAL LEAD COMPANY.

273. Manufacture. As an article of direct production, litharge is prepared in this country by two processes which are the same in principle, but are quite different mechanically. In the older and more general process the lead is placed in a low arched reverberatory furnace, the fire being on one side and separated from the melting hearth by a low brick wall, causing the flame and heat to pass above the surface of the lead. A rapid oxidation ensues, the oxide being pushed to one side by means of an iron rabble, thus exposing a fresh surface of the lead to oxidation. Pigs of lead are gradually added and the operation continued until a sufficient amount of oxide is accumulated, which is then withdrawn from the furnace, ground and levigated. The oxidizing operation is conducted at or above the melting point of the litharge. As produced by this process litharge is a buff-colored powder.

274. Cupellation Process. The other process attains the same result by the use of natural gas, and air jets play over the surface in such a manner as to sweep the molten oxide as it is formed toward the front of the furnace, and by regulating the size of the stream of molten lead which is constantly flowing in, the molten oxide flows over the lip of the basin in a steady stream into a conical shaped iron container mounted on trucks, which when full is hauled away to cool, after which the contents are removed by inverting the container; the cake is then broken up with sledge hammers, ground and air-floated to free it from metallic lead particles.

275. Other Processes. As an indirect product, litharge is produced in the metallurgy of silver, the resulting alloy of lead and silver being subjected to oxidation whereby the lead is converted into litharge, the silver remaining in the metallic condition, and is so removed. The production of litharge from acetate of lead and residual metallics has already been discussed under the Matheson process. This

litharge is entirely free from metallics. Sublimed litharge has also been mentioned in connection with the sublimed lead pigments.

276. Properties. As it occurs in commerce, litharge usually contains iron, copper, and a little silver and silica, as well as an appreciable percentage of metallic lead. Sometimes it will be found to contain lead carbonate and sulphate. If the heat has not been carefully regulated, it will contain quite a little red lead, which is a serious objection from the color maker's point of view, as the red lead is insoluble in the acetic acid which is the solvent acid for the lead in most instances in making chrome yellows and chrome greens. Litharge for storage battery use must be free from metallic lead and should not contain more than 0.006 per cent of chlorine.

277. Massicot. This oxide has apparently the same chemical composition as litharge. It is, however, much different in its physical properties, and to some extent in its chemical properties. It is the product of the first stage of the manufacture of red lead by the double firing method, and its method of preparation will be found under that heading. It is a pale greenish yellow powder of granular texture.

278. Commercial Classification. Commercially the different modifications of litharge of lead monoxide are known as

Color makers' oxides.

Enamellers' oxides.

Glassmakers' oxides.

Potters' oxides.

Rubber makers' oxides.

Varnish makers' oxides.

279. These terms, however, have partially lost their original significance, as the quality of oxide obtained in any of these industries will depend to a considerable extent on the discrimination exercised by the purchaser. Color-

makers' oxide is a crystalline oxide ground very fine, is or should be free from metallic lead and entirely soluble in dilute acetic acid. One of the leading brands of color-makers' litharge analyzed by the author gave only 0.18 per cent insoluble impurities in acetic acid. A more finely powdered sample of the same brand gave 0.70 per cent insoluble. Enamellers', glassmakers' and potters' oxides are usually the more common grades, although the purchaser may not always be aware of the fact. Iron and copper are the most serious impurities. Rubber makers' oxide is also a common oxide although the metallic lead is kept as low as possible. Varnish makers' oxide should be as free as possible from red lead. It usually contains a small amount of metallics.

280. Production of Litharge in the United States. The following figures, taken from the Mineral Resources of the United States, give some idea of the importance that the manufacture of this lead product has assumed.

Year.	Quantity.	Value.
	lbs.	
1902	25,510,690	\$1,298,343
1903	20,642,000	1,116,361
1904	16,724,448 ¹	922,919
1905	39,756,000 ¹	2,307,233
1906	37,820,000 ¹	2,551,346
1907	41,676,000	2,854,987

¹ Includes production of orange mineral.

281. Imports. A comparison with the amounts imported during this period indicates that the litharge industry is fully equal to domestic consumption.

Year.	Quantity.	Value.
	lbs.	
1902	88,115	\$2,908
1903	42,756	1,464
1904	44,541	1,500
1905	117,757	4,139
1906	87,230	3,737
1907	90,475	4,386

CHAPTER XIX.

THE OXIDES OF LEAD (Continued).

282. Early History of Red Lead. Red lead and orange mineral, while not of as ancient origin as litharge, were well known to the early Greeks and Romans. Orange mineral, which may be considered as a variety of red lead, was a well known product in the time of Pliny, who relates that it was discovered by accident through the occurrence of a fire in a house near Athens containing several earthen jars filled with white lead, it being alleged that the white lead or ceruse was in the apartments of a lady who was accustomed to use it as a cosmetic. After the fire it was found to have been changed in color to a brilliant scarlet red and was afterwards used by Nicias, a celebrated artist who lived about 320 B.C., as a new pigment, and was afterwards known under the name *cerussa usta*.

283. Early Methods of Preparation. The preparation of red lead by first drossing lead at a low temperature and then reheating the litharge or massicot thus obtained, seems to have been unknown to the ancients as they depended entirely on the product obtained by heating white lead, which according to Discorides should be "put in a new earthen vessel, best of all an Attic one, over coals, sprinkle in it powdered ceruse, stir constantly, and when it shall have acquired the color of ashes, remove and cool and so use it. But if you desire to burn it, place it powdered in a hollow platter, and having set this on the coals, stir with an iron rod until it attains the color of sandarach; then take it out and use."

284. The presence of red lead has been found in several analyses by Davy of colors obtained from the ruins of ancient Rome. Its use, however, by artists was slight and unimportant down to the time of the revival of art in Italy. But from this period its use and manufacture rapidly spread over Western Europe.

285. Development of the Industry. History does not clearly record the time that our present method of making red lead, i. e., of first drossing the metal and then reheating the oxide produced, first came into use, but it was probably prior to the beginning of the sixteenth century. It is recorded that as early as 1622, there were at least four firms engaged in the manufacture of red lead or minium in England. Smith in his "Painting in Oyl," 1676, describes the drossing of lead, forming litharge which is then treated in a furnace with constant stirring. He also adds that this red lead thus produced is used in the manufacture of drying oils.

286. Savary, in his Universal Dictionary (1751) gives a comprehensive description of the manufacture of red lead, showing that the underlying principles were well understood at that time. According to his description the lead was melted in a broad, shallow, open vessel, stirred until reduced to a gray powder, which on further treatment became the product known as "masticot." This masticot was then heated in a reverberatory furnace where it changed its hue to a fine red color and became minium or red lead. By this time red lead had become a common article of commerce and was being produced in quite large quantities by those accustomed to the manufacture of white lead, especially among the Dutch and English.

287. Early Manufacture in the United States. The exact date of the beginning of the red lead and litharge industry in the United States is not known, but probably preceded

that of the manufacture of white lead by a very brief interval. Bishop relates that there were three red lead works in operation in Philadelphia as early as 1810. The oxide industry, however, is so closely associated with the manufacture of white lead that it has almost entirely passed into the hands of the latter and there are at the present time only one or two firms who are engaged in the manufacture of oxides who are not making white lead.

288. Present Methods of Manufacture. By far the greater portion of red lead manufactured in this country is made by the two stage method. The first stage, which consists of the drossing of the lead, is conducted in a reverberatory furnace with free access of air. The heat is generated usually in two fireplaces, arranged one on each side of the rectangular drossing basin and are separated from it by means of low walls so that the flame and heated products of combustion do not come in close contact with the surface of the lead but pass close to the vault of the furnace, the lead being heated by the reflected heat from the vault, the various gases passing off through a flue situated over or at one end of the drossing basin.

289. Furnace Temperature. The temperature of the furnace must be kept within certain narrow limits, slightly above the melting point of lead, i.e., about 340° C., for if the oxide formed, which is known as massicot, is allowed to melt it undergoes a molecular change and becomes the ordinary litharge, which, as is well known, is a fixed oxide and will not take up oxygen and become red lead in the second or calcining stage.

290. The bottom of the furnace or drossing basin is more or less concave, although the low level is maintained to the bottom of the door at the front of the furnace to permit of the easy removal of unoxidized lead remaining at the end of the drossing stage.

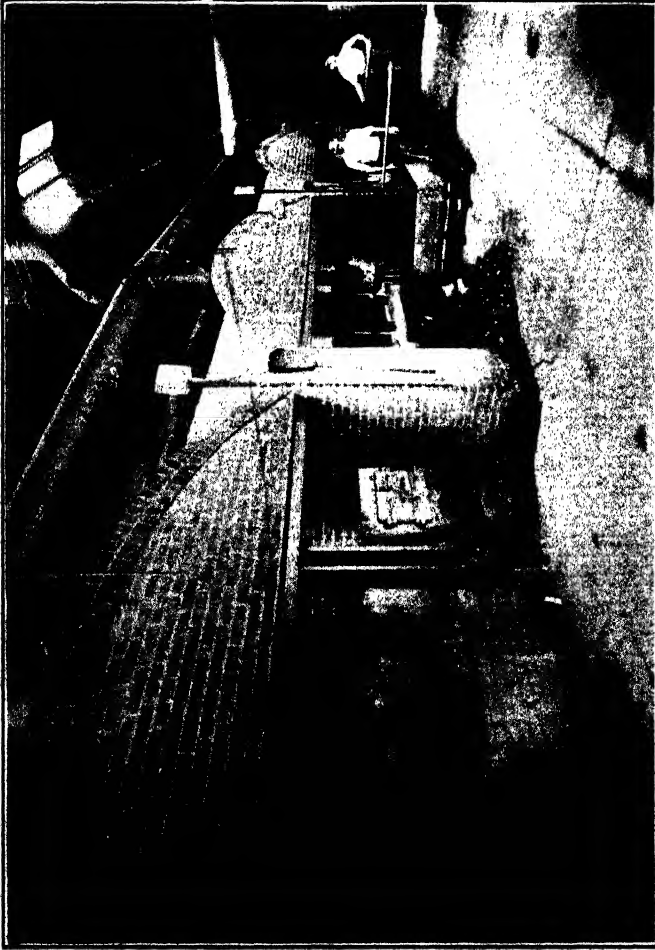


FIG. 75. — OXIDE FURNACES. — EAGLE.

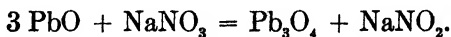
291. Drossing. The furnace is raised nearly or quite to a very dull red heat, several hundred weight of pig lead introduced, the molten metal as it forms being prevented from flowing out of the front of the furnace by a dam of dross obtained from a preceding charge. The molten lead becomes rapidly coated with a pellicle of oxide, which is raked to the front or back of the furnace by means of a heavy long-handled iron rake suspended by a chain from overhead so as to permit of easy manipulation. At intervals more lead is introduced into the furnace and the drossing operation continued for about twenty-four hours, sufficient air being introduced through the door in front. The unoxidized lead, which may constitute 15 to 30 per cent of the furnace charge, is then allowed to run off, and the massicot, which forms a friable yellow or greenish yellow mass and corresponds to the formula PbO , is raked out into iron carts, cooled, ground and floated to free it from metallic particles, dried and introduced into the calcining furnaces, which are similar to the drossing furnaces or else of the muffle type. The collected residues, consisting of coarse dross and granules of metallic lead, amounting to from 10 to 30 per cent of the furnace charge, are dried and again drossed.

292. Coloring. For the production of the deepest red tones a muffle furnace is used, for if the flame is allowed to come in contact with the product, the tint is injured. A suitable current of air is admitted and the mass frequently raked in order to assist the absorption of oxygen and to develop the tint, the operation requiring upwards of forty-eight hours, samples being taken at intervals until the desired tint is obtained. The red lead is then removed, cooled, and if not sufficiently fine, is ground. As in the drossing stage, the temperature in the second or calcining stage must be carefully regulated and kept within certain narrow limits.

293. The brightness, deepness, and beauty of color depend on the care exercised in calcining and are not wholly influenced by the absorption of oxygen, but more especially by the particular molecular condition or structure of the product, and this is only obtained within a certain narrow range of temperature.

294. Modern Improvements. Various modifications have been developed which have simplified and shortened the furnacing operation as applied to red lead and also litharge. They have not, however, proven sufficiently economical as to have materially restricted the use of the two-stage process. Among these various improvements may be mentioned the use of mechanical stirrers, rotary drossing furnaces, use of currents of superheated air, etc.

One modification, however, has proven financially successful, owing to the production of a valuable by-product, nitrite of soda, much used as a diazotizing agent in the manufacture of para reds and other similar colors. This modification is based on the fact that sodium nitrate will easily give up one atom of oxygen, becoming sodium nitrite and the liberated oxygen immediately combining with metallic lead to form an oxide easily convertible into red lead, or it may be made to convert massicot rapidly into red lead, according to the following equation:



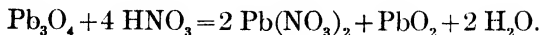
295. The Nitrate Process. Many types of furnaces have been designed in order to bring about the above reactions. In one modification for the production of a massicot or litharge the sodium nitrate is melted in a large iron pot, which is kept at about 340° C., or at about the melting-point of lead. The lead is added in the form of thin plates until in slight excess of the calculated quantity. The temperature is kept up for about 20 to 30 minutes after all

of the lead has been added, or until the yellow mass has turned to a brownish color. The liquid mass is then removed, extracted with water to dissolve out the sodium nitrite, the solution of which is evaporated and the nitrite crystallized out. In another modification a circular iron pan about 4 feet in diameter and 18 inches deep is used. The pan is provided with a mechanical stirrer and is placed on a perforated arch; 200 pounds of nitrate is added and when melted about 300 pounds of lead added; the mass is then agitated until oxidized, when 50 pounds of nitrate and 350 pounds of lead are added. The heat is maintained for 30 to 45 minutes after apparent action has ceased.

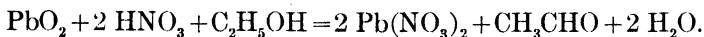
296. The molten contents are poured into 120 gallons of warm water, the sodium nitrite going into solution. The solution is drawn off into a large tank, neutralized with just sufficient sulphuric acid, the settled liquor concentrated in iron pans or multiple effect evaporators to about 45° B., and allowed to crystallize. The nitrite thus obtained should be at least 96 per cent pure. The oxide is freed from all traces of nitrite by washing in an agitated washing box, dried and treated as desired.

297. Properties. When properly prepared red lead is a brilliant scarlet red crystalline powder containing 90.66 per cent lead and 9.34 per cent oxygen, the theoretical chemical increase in manufacture being 10.3 per cent. In actual practice, especially in the double furnacing method, this is not obtained, 7 to 8 per cent representing the increase obtained, as there is considerable loss of oxide dust through the flues. Its specific gravity varies between 8.6 and 9.1. On heating, it assumes a more brilliant color, passing through violet to black, but on cooling regains its original tint. It is readily soluble in hot hydrochloric acid with a copious evolution of chlorine. In nitric acid it is only partially soluble, lead nitrate and insoluble

lead dioxide being formed according to the following equation:



The addition of a little alcohol and further boiling will, however, effect complete conversion into lead nitrate, the alcohol being reduced to acetaldehyde.



298. Adulteration. Aside from purity, red lead is valued according to depth and brilliancy of tone, the production of the deepest shades being considered a valuable trade secret. The adulterating of red lead with brick dust and oxide of iron has passed into disuse and when sold simply as red lead it will usually be found to be commercially pure. There are, however, numerous combination red leads on the market in which the lead has been brightened and made more brilliant by the use of an organic color, such as eosine, precipitated on an inert base like barytes. These combination red leads are usually sold slightly below red lead prices, and while they serve their purpose excellently, the color does not permanently maintain its brilliancy.

299. Selection for Vermilions. Red lead which is intended to be ground with linseed oil and placed on the market in sealed packages which may not be used for some months, or red lead which is to be used in the manufacture of vermilions, should be selected with regard to litharge content, as there is great danger of hardening in the package, resulting in financial loss and much inconvenience. A simple, rapid test and yet sufficiently accurate test for the purpose is to digest 2 grams of the sample in 50 c.c. of a 10 per cent neutral solution of lead nitrate on the water-bath for

about 30 minutes. The free litharge will be taken up into solution, and the undissolved residue collected on a Gooch crucible, washed, dried and weighed. A red lead containing 12 per cent of soluble oxide is not suitable for the above purposes. The limit for orange mineral may be taken as 6 to 8 per cent under similar treatment. In fact, there are only one or two grades of red lead in this country which will pass these requirements.

300. Red lead for glassmaking must be free from commercial impurities, especially copper and iron. Red lead for match making is valuable in proportion to the peroxide it contains, which may vary from 28 to 33 per cent.

301. Orange Mineral. This product may be considered as a debased form of red lead, as on long exposure to light it darkens. The empirical formula of orange mineral is the same or closely the same as for red lead. It is prepared by calcining white lead or the neutral carbonate of lead. The finest tints are prepared by heating the particles of white lead obtained from the foam from the washing and settling tanks in the manufacture of white lead. Much of the orange mineral made in this country is prepared by calcining the more or less basic carbonate of lead obtained by dissolving litharge in acetic acid, forming a basic acetate, which is then carbonated, dried and calcined in the same style of furnace as massicot, at a carefully regulated temperature, the evolved water and carbon dioxide passing up to the flue. Orange mineral is less dense than red lead, having a specific gravity of about 6.95, and is valued according to the depth and brilliancy of its bright orange shade.

302. Production and Imports of Red Lead.¹

Year.	Production.		Imports.	
	Quantity.	Value.	Quantity.	Value.
	Pounds.		Pounds.	
1902	23,338,252	\$1,263,112	1,075,839	\$37,383
1903	17,664,000	1,022,754	1,152,715	40,846
1904	18,340,731	1,076,131	836,077	30,115
1905	32,756,000	2,049,888	704,402	26,553
1906	27,616,000	1,924,288	1,093,639	50,741
1907	40,156,000	2,802,454	679,171	35,959

303. Production and Imports of Orange Mineral.¹

Year.	Production.		Imports.	
	Quantity.	Value.	Quantity.	Value.
	Pounds.		Pounds.	
1902	1,973,521	\$139,349	997,494	\$49,060
1903	1,302,000	100,693	756,742	36,407
1904	766,469	37,178
1905	628,003	31,106
1906	770,342	42,519
1907	1,338,000	129,410	615,015	37,793

Report, Production of Mineral Paints, 1902-1907.

CHAPTER XX.

THE LEAD CHROMATES.

304. Varieties. The manufacture of chrome yellows, orange and reds has increased greatly within the last few years, and now amounts to a yearly production of several thousand tons. Based on simple chemical principles and requiring a comparatively small financial outlay for equipment, their manufacture has not been restricted to a few firms solely engaged in the color business, and there are at the present time at least a dozen of the larger paint houses who prepare their own chrome pigments. The various shades of these chrome pigments may be classified according to common use as follows:

Canary yellow.

Canary yellow, deep.

Lemon yellow.

Chrome yellow, medium.

Chrome yellow, orange.

Chrome yellow, deep orange.

American vermilion, Chinese scarlet, etc.

305. Tinting Strength. Although prepared by simple chemical processes, the production of uniform tints of high tinting strength is by no means an easy undertaking, as a careful examination of the chrome colors offered to the trade will show. Exactness of method and careful attention to details are the essential elements of success. Two chrome yellows may appear to possess identically the same tint and tone, yet when reduced with equal quan-

tities of a white pigment, e.g., white lead, one may be found to possess 25 per cent more strength than the other and will still maintain a clear yellow tone, while the other will appear dirty or may pass over into another tone or color altogether. Chemically these yellows may be the same, and the difference is therefore due to the methods of manipulation.

306. Presence of Lead Sulphate. The lighter colored chrome yellows contain besides neutral lead chromate a varying percentage of sulphate of lead, the function of which is to lighten the tint. It has been a much discussed question as to whether this sulphate of lead exists free or as a sulpho-chromate. In the opinion of the writer the combination is very similar to that in zinc-lead, which is very closely on the border line between chemical combination and mechanical mixture, due to the exceedingly close intimate contact of the component particles, and the relations which apply under these circumstances are not clearly understood.

307. Raw Materials. The source of the lead in the manufacture of these yellows is either lead nitrate or basic lead acetate; the source of the chromium being sodium or potassium dichromate and the sulphate radical from sulphuric acid or sulphate of soda. Lead nitrate produces a much richer, clearer, and stronger chrome yellow than the acetate, but unfortunately these advantages are partially offset by the higher cost of the lead content in lead nitrate than of the lead content in basic lead acetate, and most color houses, therefore, prepare their yellows from the acetate, which they make themselves from ordinary litharge or from color makers' oxide and commercial 56 per cent acetic acid. While it is possible to prepare on a commercial scale any of the several basic acetates, the one most commonly used corresponds to the formula $Pb(C_2H_3O_2) \cdot PbO$, although the tribasic acetate,

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{PbO}$, is used to some extent, more especially in the deeper yellows. Each is prepared by first forming the neutral acetate and then digesting with the calculated quantity of litharge to form the desired acetate. The litharge used for this purpose should be selected with regard to freedom from metallic lead and red lead, both of which are substantially insoluble in the acetic acid used and would therefore affect the quality of the color product.

308. Sodium Bichromate. Either the sodium or potassium bichromate may be substituted for the other in chrome yellow formulas provided the quantities required are calculated according to the molecular weights; both used with the same lead salt will produce the same tint and strength. Many color makers, however, prefer to use the potassium salt, although it costs about a cent a pound more, because it does not attract moisture from the atmosphere on standing as does sodium dichromate. This absorption of moisture decreases the apparent chromium content of the salt, making it difficult to follow the working formula exactly. A number of color houses purchase their sodium dichromate in comparatively tight barrels and prepare a large quantity of stock solution at a time and thus avoid the above difficulty.

309. Precautions to be Observed. Especial precautions must be observed in the preparation of the lighter colored yellows, in order to avoid their darkening during manufacture. These precautions may be summarized as follows:

1. Use of very dilute solutions.
2. Continuous agitation during precipitation.
3. Maintenance of low temperatures, i.e., as near room temperature as possible.
4. Rapid manipulation during the precipitation and especially during the subsequent washings.

310. Secret Formulas. Nearly every color maker has his own cherished formulas which he guards with the greatest care. In the majority of instances his efforts in this direction are needless, as the essential details are well understood by all of his professional brothers. Among these details may be mentioned the advantage of using an excess of about five per cent of dichromate above what is required for actual combination, the tone and strength of the resulting color being much improved. In the manufacture of lemon yellows it is customary to neutralize the dichromate with the calculated quantity of sodium carbonate to form the neutral chromate before precipitating. In order to obtain the light clear tone required of a canary yellow a small quantity of tartaric acid is added to the dichromate solution. A yellow obtained by this method must be handled with care, as a number of instances are on record where it has undergone a spontaneous decomposition.

311. The amount of sulphuric acid or sulphate of soda used will depend upon the lightness or paleness of the tint desired. However, as sulphate of lead is cheaper than chromate of lead, some color makers, who are able to produce exceptionally strong yellows, will let them down with sulphate of lead until of only average strength, thereby securing an increased profit. Twenty to thirty per cent will represent the lead sulphate content of the usual run of lemon yellows. Instead of using a soluble lead salt entirely, it may be partially replaced with white lead, a portion or all of which may undergo conversion into chromate or sulphate as may be desired, and this affords another way of reducing the cost of a chrome yellow, although at the expense of its strength. In fact it is difficult, if not impossible, to produce as strong and clear a yellow with the use of white lead as without.

312. Practical Formulas. The following practical working formulas, which can easily be adapted to tubs of any desired size, clearly illustrate the points above discussed.

Material.	Lemon yellow.		Canary yellow.		Canary yellow, deep.		Medium yellow.	
	lbs.	oz.	lbs.	oz.	lbs.	oz.	lbs.	oz.
Lead nitrate.....	100	00	100	00
Litharge.....	100	00	100	00
White lead.....	300	00
Acetic acid (56%).....	43	12	43	12
Potassium dichromate.....	40	00
Sodium dichromate.....	43	12	60	00	61	4
Sulphuric acid.....	40	00
Sodium sulphate (crystals).....	80	00
Sodium carbonate (dry).....	17	10
Tartaric acid.....	1	00

313. Precipitation. The amount of water required by these formulas depends somewhat upon the capacity of the tubs and the output required of the color maker. It is of course understood that the chromium solution is run into the lead solution always, and any sulphate-forming materials or modifying materials like tartaric acid are added to the chromate solution before precipitation. The more closely the four rules above referred to are followed the more nearly uniform and the stronger will be the yellows produced.

314. Orange Chrome Yellows. The lighter the color of the yellow produced, the more amorphous and fluffy it is, and in passing down the list to the deeper colors, it will be noticed that they become more and more crystalline the more orange or red the color, the deepest colored American vermilion being exceedingly crystalline. The color of these compounds, therefore, depends partly on the physical structure, but more especially in the darker chromes upon the formation of a basic lead chromate, which instead of

being yellow is of a decidedly red color. The orange chromes may be considered as mixtures of the neutral chromate and basic chromate. They are prepared by heating the chromate after formation with caustic soda or lime, the amount of lime or soda and the length of heating determining the color produced. The following working formulas will serve to illustrate the manufacture of the medium orange and deep orange shades.

Materials.	Orange.		Deep orange.	
	lbs.	oz.	lbs.	oz.
Lead nitrate.....	100	00	100	00
White lead.....	80	00	100	00
Sodium dichromate	51	12	75	8
Calcium oxide.....	10	00	17	00

315. Addition of the Calcium Oxide. The calcium oxide is added in the form of a very thin paste as hydroxide, after the chromate is precipitated. The mass is then heated until the desired tint is produced, more lime being added if necessary. Although lime is cheaper than caustic soda, the economy of its use is somewhat doubtful, as the reaction with caustic soda is very much easier to control.

316. The orange chromes will not darken nearly as much during the washing and drying processes as the lighter yellows, nevertheless due care should be exercised in their preparation.

317. American Vermilion. This pigment, known to the trade under various names such as Chinese scarlet, Persian red, etc., is a very heavy, strongly crystalline scarlet red pigment. Owing to the fact that it settles very rapidly when mixed with oil and is very difficult to grind owing to its becoming very much lighter in color due to the crushing of the crystals, together with its comparatively high price,

it has quite largely passed out of use, although as a rust resisting pigment for iron and steel painting it is almost without an equal. Its proper production is attended with considerable difficulty, and it is now prepared by only a few firms, who have practically a monopoly of the business owing to the fire and brilliancy of their product.

318. White lead is usually the lead salt used in the production of American vermilion, a selected grade being used for this purpose. Some authorities consider a white lead high in hydroxide as the most suitable, but according to the experience of the author the physical structure of the white lead is the more important consideration. White lead, composed of very fine particles, as Carter or Mild process, will not yield a deep American vermilion, whereas a specially prepared lead, containing 85 to 90 per cent carbonate, and which has a coarse crystalline structure, will yield an excellent vermilion. When it is considered that the larger the crystals the deeper the tint, this view is the natural one.

319. Preparation. This pigment may be prepared according to several methods. The following formula, however, with careful manipulation will give excellent results. One hundred pounds of white lead is ground into a very thin, smooth paste, and run into a dilute boiling solution of potassium dichromate, 28.5 pounds in 60 gallons of water; the dichromate having been neutralized with crystallized sodium carbonate, about 27 pounds being required. The boiling is continued for about ten minutes or until the precipitate attains the desired shade. It is allowed to settle, the supernatant liquid removed, the precipitate washed and then treated with dilute sulphuric acid (1 : 10), an amount equivalent to about four per cent of the weight of the chromate produced being used. The mass is slowly stirred until the desired brilliancy is obtained. The acid is

then immediately neutralized with soda. The now brilliant vermilion is washed and dried in a vacuum drier or on a chalk bed. Some manufacturers use caustic soda or slaked lime in place of the sulphuric acid, but the reaction is more difficult to control.

320. Care in Grinding. Care should be exercised in the drying of all of the chrome pigments, as temperatures above 60° C. are liable to cause alteration of shade. The grinding of these colors also requires considerable attention. The lighter colors may be ground in a fairly tight mill; the medium yellow, if from acetate, and the orange shades must be ground in a loose mill, while the vermilions cannot be put through a grinding process at all without destroying their color.

CHAPTER XXI.

LITHOPONE.

321. Early History. This pigment, the best grades of which contain about 28.5 per cent zinc sulphide, 1.5 per cent zinc oxide and 70 per cent barium sulphate, has been in extensive use only a comparatively few years. Its origin dates back to about 1874, in which year a patent was taken out by a J. B. Orr in England for the manufacture of a zinc sulphide pigment under the name of Orr's White or Orr's White Enamel. Orr prepared his pigment by calcining an intimate mixture of barytes and charcoal for several hours and leaching out the resulting barium sulphide with water.

322. The solution obtained was divided into two portions; to one a solution of zinc chloride was added, resulting in the formation of zinc sulphate and barium chloride. Without separating the precipitated sulphide of zinc, the solution was then treated with the remaining portion of barium sulphide, and a sufficient amount of zinc sulphate solution, the combined precipitates washed, filtered, dried, calcined, and while hot thrown into cold water, which made the product more dense, i.e., gave it greater body. This was followed, in 1875, by another patent by Griffith, who made use of the mixture of waste sulphides, calcium and sodium obtained in the Leblanc soda process. Since that date numerous improvements have been made and the manufacture of zinc sulphide whites has been successfully introduced into this country, the product being sold under such fanciful names as Lily white, Diamond White, Snow White, Ponolith, Beckton White, etc.

323. Zinc Sulphide. Zinc sulphide itself may be made by adding ammonium sulphide to an alkaline solution of any zinc salt, giving a white, slimy precipitate of the sulphide of zinc, which, however, cannot be used by itself as a paint pigment, but must be intimately mixed with an inert base like barytes. According to Bell, the most favored method of manufacture at the present time is quite closely that devised by Orr.

324. Preparation of Zinc Sulphate. The zinc sulphate is prepared in several ways. In Germany it is prepared directly from ore; in the United States, by dissolving metallic zinc or zinciferous by-products in sulphuric acid. The practice in one works is to burn the zinc out of scrap brass, the copper being left behind while the zinc passes as a white fume (ZnO) into settling chambers, and is collected and dissolved in sulphuric acid, the solution being properly purified before being used for lithopone.

325. Preparation of Barium Sulphide. The barium sulphide is usually prepared by heating an intimate mixture of about four parts crude barytes and one part of a very low ash coal in a revolving furnace for two to three hours at a bright red heat, a very slight amount of air being admitted. Sixty to seventy per cent of the barytes used is converted into soluble sulphide, the rest remaining as insoluble barium carbonate, which, after being entirely freed from sulphide by washing, is converted into barium nitrate or barium chloride as desired.

326. Instead of coal other carbonaceous materials have been proposed, such as coal tar, which is incorporated with the barytes in a chaser before being charged into the furnace. Potato starch has also been used and one to two per cent of the weight of the charge of calcium chloride added, which gives a semi-paste in the furnace.

327. Precipitating and Calcining. The calculated quan-

tity of barium sulphide is added in the precipitating tub to the requisite amount of zinc sulphate solution when an intimate mixture of zinc sulphide and barium sulphate is obtained as a precipitate, which is then placed in a rotary furnace and calcined at a high heat. The calcined mass is thrown into water, ground in stone mills, washed until the wash water is neutral, settled, filter pressed and dried on trays in drying rooms and finally powdered by running through a pulverizer.

328. Physical Properties of Lithopone.¹ The body of this product is almost equal to that of white lead, and Green Seal lithopone, as made in this country, is equal to that of French process zinc white. The brands sold as Red Seal, Yellow Seal, Blue Seal, etc., are simply mixtures in the dry way of Green Seal lithopone and ordinary barytes. The higher the calcination, the better is the color and the less oil is required for grinding or mixing the pigment and the better it will work under the brush. When it is less highly calcined, the pigment, while favored in some industries, is unfit for the use of the painter, because it works slimy and tends to thicken, requiring too great a quantity of thinners, thereby losing body or opacity.

329. Reductions. Comparing the percentage of oil required for 100 pounds of white paste of similar consistency, we may place the figures as follows:

Pure white lead.....	9½ per cent.
Green Seal lithopone.....	12 per cent.
American zinc oxide.....	14 per cent.
French process zinc.....	15 per cent.

330. To reduce the paste so ground to the proper working consistency with a thinner consisting of oil

¹ Oil, Paint and Drug Reporter, LXXII, No. 21, page 38.

and driers would require for 100 pounds paste in the case of

Pure white lead	4 gallons.
Green Seal lithopone	6½ gallons.
American zinc oxide	8 gallons.
French process zinc	8½ gallons.

331. The relative percentages of dry pigment and vehicle in the paints so prepared would then figure out as follows:

	Pigment.	Liquid.
	Per cent.	Per cent.
Pure white lead paint	71.28	28.72
Green Seal lithopone paint . . .	58.50	41.50
American zinc white paint . . .	53.10	46.90
French process zinc paint	51.30	48.70

332. Comparison with White Lead. The chief points in favor of lithopone as compared with white lead and zinc white are the greater opacity and greater elasticity as compared with zinc oxide, and its inertness in the presence of sulphur gases which tend to discolor white lead paint. On the other hand lithopone has one drawback, that of blackening when exposed to the sun before it has become thoroughly dry. Also when mixed with white lead or colors containing a copper or lead base, it will blacken, due to the formation of sulphide of lead. This is also liable to happen when a drier containing lead salts is used in the oil paint.

333. Grades of Lithopone. As before stated lithopone is graded according to its zinc sulphide content, other considerations being equal. In Germany four grades are usually offered: Green Seal, which consists of approximately one part zinc sulphide to two parts barium sulphate; Red Seal, consisting of one part of zinc sulphide to three parts

barium sulphate; Blue Seal, one part of zinc sulphide and four parts barium sulphate; and Yellow Seal, one part zinc sulphide and five parts barytes. It is asserted by some German authorities that the addition of ten to fifteen per cent of calcium carbonate in the grinding of lithopone in linseed oil reduces the liability of the lithopone to blacken on exposure to light. In this country, also, several patents have been granted for improvements in preventing darkening. As lithopone is largely used in the manufacture of enamels for furniture, bedsteads, etc., permanency of color and density of product as well as original whiteness are prime considerations.

334. Manufacturers. As far as the writer has been able to ascertain the following list represents the manufacturers in this country.

No.	Company.	Location.
1	Beckton Chemical Company.....	Beckton, N. J.
2	Cawley, Clark & Co.....	Newark, N. J.
3	Cheeseman Chemical Company.....	Scranton, Pa.
4	Excelsior Manufacturing Company..	Newport, Del.
5	Grasselli Chemical Company.....	Grasselli, N. J.
6	Harrison Bros. & Co.	Philadelphia, Pa.
7	Heller & Mertz.....	New York.
8	Krebs Pigment & Chemical Company	Newport, Del.
9	New Jersey Zinc Company.....	Palmerton, Pa.
10	N. Z. Graves & Co.....	Philadelphia, Pa.

335. Production. The production of lithopone is increasing rapidly in this country, indicating that consumption is increasing steadily, as in 1906, 4,300 tons, valued at \$311,500, were manufactured as against 10,275 tons, valued at \$750,350 in 1907.

CHAPTER XXII.

PHYSICAL PROPERTIES OF WHITE LEAD.

336. Amorphous Character of White Lead. Chemical analysis cannot be relied upon entirely for information regarding the amorphous character of white lead, and it is a mistake to assume that because the ratio of carbonate to hydroxide found agrees closely with the theoretical the sample in question is always a desirable product, for it is by no means rare to find crystalline carbonates present in quantity when a chemical analysis will show less than the theoretical amount of carbonate. A close examination with the microscope and a close comparison, microscopically, with the accepted standards should always be made, and the results of such examination should be considered of equal value to the data obtained chemically.

337. Color. The color or whiteness of white lead can only be judged by comparison with an accepted standard kept for that purpose. The two leads, standard and sample, are weighed out in gram lots on to a large glass plate, twelve drops of bleached linseed oil added to each and rubbed up thoroughly and matched up on a microscope slide, the leads being spread out evenly. The color should be judged from both sides of the glass. After comparing the color, place the slide in the steam oven for two hours. This will give some idea as to the amount of yellowing that will occur when the lead is used in painting. This defect is particularly marked in pulp leads.

338. Cautions to be Observed. If the particles of one of the leads are much finer than those of the other, the above

test may appear deceptive, as the surface of the former will have a considerable luster, due to the smoothness of the surface and its apparent oiliness. This condition may be observed at once if the slide be held in different positions with regard to the source of light, and the sample under examination can often be made to appear darker or lighter than the standard at the will of the operator. In order to get a true comparison under such conditions, a small amount of each lead should be placed side by side on the edge of a piece of cardboard or blotting paper and then flattened out uniformly with one motion of a palette knife. The cardboard or blotter will after a short time have absorbed sufficient oil to render the comparison of the whiteness of the two surfaces fair.

339. Opacity. Two grams each of the sample and standard are very carefully rubbed up with 0.01 gram of a high grade of ultramarine blue and twenty-four drops of bleached oil. This operation should be conducted on a large sheet of glass, using a flat-bottomed glass pestle or muller. A uniform pressure and the same number of grinding motions should be used with regard to sample and standard. After a certain number of motions the material should be gathered up with a sharp-edged spatula and again ground out, until the operator is satisfied both leads have been treated exactly alike. Instead of a glass muller a palette knife may be used if sufficient care is observed.

340. The more strongly the lead is colored, the weaker it is in hiding power or opacity. Adding weighed amounts of lead until the colors are of equal depth will show the ratio between the two. Some leads are so crystalline that a great difference in opacity is observable.

341. Oil Requirements and Reductions. The amount of oil required in grinding white lead can only be determined.

by experiment, preferably in a mill of the regular size. In determining the reduction which the various white leads and pastes will stand, some convenient method should be adopted for calculating the amount of oil used in gallons per hundred pounds of paste. One of the simplest schemes is to weigh out the leads or pastes in $12\frac{1}{2}$ ounce quantities or multiples thereof. Then each ounce of oil used is equivalent to one gallon per hundred pounds of paste.

One gallon is equivalent to 128 ounces.

One hundred pounds are equivalent to 1600 ounces.

$$1600 \div 128 = 12.5.$$

If larger amounts were required, the necessary multiple of $12\frac{1}{2}$ should be used and the other figures increased accordingly.

342. In this way the necessary quantities of turpentine and drier can be readily calculated and measured out. For instance, if a specification to be tested out read,

100 pounds white lead,
7 gallons raw linseed oil,
 $\frac{1}{2}$ gallon turpentine,
 $\frac{1}{8}$ gallon turpentine drier,

the above scheme would call for

$12\frac{1}{2}$ ounces white lead,
7 ounces raw linseed oil,
 $\frac{1}{2}$ ounce turpentine,
 $\frac{1}{8}$ ounce turpentine drier.

343. Laboratory Tests for Opacity and Covering Power.

It is oftentimes desirable to conduct small laboratory tests for opacity and spreading. A very convenient method is to lay off equal squares on a stiff cardboard one side of which has been painted black; then with standard and

sample reduced alike, apply equal amounts, and brush out evenly with a carefully selected brush. The cards should be allowed to dry in a place free from laboratory fumes or gases and should be exposed to as strong a light as possible. It should be remembered that in subdued light, or if the cards are allowed to remain on top of each other after drying, the tests will rapidly turn yellow, due to the yellowing of the linseed oil. This fact should always be taken into consideration when judging the whiteness. If the standard and sample will not stand the same reductions the above scheme will apply equally well in judging body obtained and amounts used.

344. Microscopical Measurements. The actual determination of the size of the individual particles of white lead is a difficult task, as they tend to agglomerate together, rendering them apparently larger than they really are. However, this danger may be avoided by taking a small quantity of the lead and working it out very carefully with a drop of linseed oil on a microscope slide until thorough incorporation is secured, then gradually incorporating one or two drops of petroleum spirits, such as is commonly used as a substitute for turpentine, until the particles are spread over a sufficient area for suitable examination under the microscope.

345. Determination of the Specific Gravity. Formerly the determination of the specific gravity of a pigment was deemed very useful in calculating the exact volume which a specified weight of pigment and oil would occupy. But actual demonstration has proven that this is not the case. The "bulking" figure of a pigment in oil depends much on its physical structure and the method of incorporation with the oil. For a great many purposes however, the knowledge of the specific gravity is very desirable.

346. The determination is best accomplished by the use of the pycnometer or specific gravity bottle; the 25-c.c. size provided with thermometer is the most suitable. The weight of the pycnometer, thoroughly cleaned and dried, is determined. The pycnometer is then filled with pure distilled water at a temperature which has been definitely decided upon; 15.5° C. (60° F.) or 22° C. (average room temperature) are the most usual temperatures. The pycnometer with contents is then weighed and the weight of the water obtained by subtraction. The pycnometer is then emptied, thoroughly dried, cooled and filled with turpentine; flask and contents must be of the same temperature as in preceding case. The weight of the turpentine is obtained, and this weight, divided by the weight of the water, gives the specific gravity of the turpentine at that temperature.

347. The pycnometer is then emptied, the inside of the neck wiped dry, a small cone of paper inserted and a carefully weighed amount of pigment, 5 to 10 grams, introduced without loss into the pycnometer, which is then about two-thirds filled with some of the same turpentine above referred to. By careful agitation and the use of a platinum wire, all of the air bubbles that may be present in the pigment are eliminated, the cap and thermometer placed in position and the flask allowed to stand fifteen minutes to half an hour in order to secure proper penetration into the pigment particles. The pycnometer is then filled with the turpentine, brought to the proper temperature and weighed, and the specific gravity of the pigment determined as by the following example:

Weight of pycnometer	24.8065 grams
Weight of water at 22° C.	25.1100 grams
Weight of turpentine at 22° C.	21.7202 grams

$21.7202 \div 25.1100 = 0.8650$, specific gravity of turpentine at 22° C.

Weight of pigment taken	10.0 grams
Weight of pigment (plus above weight of turpentine)	31.7202 grams
Weight of pigment and turpentine together in flask	30.4135 grams
Weight of turpentine occupied by 10 grams of pigment	1.3067 grams

$10.0 \div 1.3067 = 7.653$, specific gravity of pigment as compared with turpentine.

$7.653 \times 0.865 = 6.62$ (approximate), specific gravity of pigment as compared with water, the accepted standard.

348. Turpentine, owing to its mobile nature, is preferable to water as a medium determining specific gravities of pigments, especially as some white leads contain traces of oil.

349. Displacement in Oil. The volume that a pigment will occupy in linseed oil or other vehicles is dependent to certain degree on the nature of the vehicle, the physical structure of the pigment and the method of incorporation. For instance a mixture of white lead and zinc oxide incorporated with linseed oil in an ordinary mixer and run through a mill will occupy an altogether different volume than if the mixture was thoroughly chased under heavy pressure before grinding. Likewise the determination of the "bulking" figure, so-called, of a pigment in linseed oil will be much different if determined by simple displacement accompanied by suitable agitation, than when the pigment is thoroughly ground with the oil, under considerable pressure. The following table, prepared by the author, clearly shows this difference.

350. "Bulking" Figure or the Number of Pounds required to displace One Gallon (231 Cubic Inches) of various Lead and Zinc Pigments.

No.	Name of pigment.	Simple.	Grinding	Displace-
		displace- ment in linseed oil.	in linseed oil.	ment in turpen- tine.
		Lbs.	Lbs.	Lbs.
1	Dutch process white lead.....	67.30	55.86	80
2	Carter white lead.....		55.90	
3	Mild process white lead.....	54.74	45.90	78.88
4	Matheson white lead.....		33.90	
5	Sublimed white lead.....	43.85	51.60	63.80
6	Zinc lead white.....	49.00	49.81	48.70
7	Zinc oxide.....	55.30	47.14	44.90
8	Lithopone.....	38.30	35.29	34.60
9	Chrome yellow, light.....	60.66	50.57	11.40
10	Chrome yellow, medium.....	45.24	44.22	10.70

351. **The Determination.** The displacement figures in raw linseed oil were obtained by weighing the pigment into a pycnometer, about one-half full of oil, incorporating as thoroughly as possible with a platinum wire, placing on top of steam oven for several hours in order to secure better penetration in and among the pigment particles, and finally cooling, making to volume and weighing in the usual manner. The "bulking" figures obtained by grinding were secured by taking from 100 grams in the case of heavy pigments, to 25 grams for the lightest pigments and grinding thoroughly with sufficient oil to make a thin smooth paste, in a glass mortar, using considerable pressure and the greatest possible care to obtain an even grind, finally transferring with the aid of a sharp spatula to a 100-c.c. pycnometer, removing the last portions from the mortar with more oil, allowing to stand on top of the steam oven for several hours for removal of all air bubbles, cooling, making to volume and weighing. For ease in com-

mercial calculations $7\frac{5}{8}$ pounds of raw linseed oil and 7 pounds of turpentine were considered as equivalent to 1 gallon. A small-necked 100-c.c. Erlenmeyer flask, calibrated by the author, was used by him for the pycnometer, as its shape was more convenient for the purpose than the ordinary type of pycnometer.

CHAPTER XXIII.

PRACTICAL TESTS.

352. The North Dakota Paint Tests. In 1907, the North Dakota Experiment Station, under the direction of E. F. Ladd and the author, undertook an extensive series of practical paint tests covering a large number of mixed paint formulas and a number of the leading brands of white leads and zinc pigments. These tests were placed on the test fences illustrated in this connection, a description of which may be found in the chapter on Practical Testing Out of Paints in the author's work on Analysis of Mixed Paints, Color Pigments and Varnishes. The reductions and applications of these paints were conducted with extreme care and the following figures with regard to the reductions employed and areas covered, as calculated from Bull. No. 81, and the Experiment Station records may be of interest.

353. Reductions. Early in 1908, the editor of one of the leading paint magazines sent out an extensive inquiry to the painters throughout the country regarding the reductions which they advised with white lead, on both old and new work and on various kinds of wood. The author had the opportunity of examining the replies received, which were numerous, and he was much impressed with the lack of agreement. In fact it was difficult if not impossible to formulate from them any general rules or principles.

The reductions used on the North Dakota tests for the lead and zinc pigments were arrived at after numerous



FIG. 76.—EXPOSURE FENCES. — NORTH DAKOTA. — WEST SIDE.

joint experiments by Mr. J. B. Campbell, the well-known paint expert, Mr. Nelson, a painter of wide experience, and the author, and as the materials applied have shown very high service values, having been exposed for upwards of two years, without much apparent deterioration, these reductions may be regarded as very satisfactory. It is to be noted that the work was three coat over the kinds of wood indicated, the time of application being the middle portion of the summer.

354. Red Seal, White Lead, Eagle White Lead, Carter White Lead and Sublimed White Lead.¹

	First coat.	Second coat.	Third coat.
White lead.....	100 lbs.	100 lbs.	100 lbs.
Raw linseed oil.....	5½ gal.	3 gal.	3 gal.
Turpentine.....	¼ gal.	¼ gal.
Drier.....	¼ gal.

355. Matheson White Lead.¹

	First coat.	Second coat.	Third coat.
White lead.....	100 lbs.	100 lbs.	100 lbs.
Raw linseed oil.....	8 gal.	4 gal.	4 gal.
Turpentine.....	¼ gal.	1 gal.	¼ gal.

356. Zinc-Lead White.

	First coat.	Second coat.	Third coat.
Zinc lead.....	100 lbs.	100 lbs.	100 lbs.
Raw linseed oil.....	5½ gal.	4 gal.	3 gal.
Turpentine.....	¼ gal.	¼ gal.
Drier.....	¼ gal.

¹ Bulletin No. 81, North Dakota Experiment Station.

357. Mild Process White Lead.

	First coat.	Second coat.	Third coat.
No. 1. Double chased			
White lead.....	100 lbs.	100 lbs.	100 lbs.
Raw linseed oil.....	6 gal.	4 gal.	3½ gal.
Turpentine.....	½ gal.	1 gal.	½ gal.
Drier.....			⅛ gal.
No. 2. Mixed and ground			
White lead.....	100 lbs.	100 lbs.	100 lbs.
Raw linseed oil.....	6 gal.	4 gal.	3½ gal.
Turpentine.....	½ gal.	½ gal.	½ gal.
Drier.....			⅛ gal.

NOTE.—No. 1 was double chased only, being allowed to sweat for 24 hours between chasings; 92 pounds lead, 8 pounds oil; consistency medium soft. No. 2 same proportions of lead and oil, but put through ordinary mixer and ground in 30-inch mill; consistency stiff.

358. New Jersey Zinc Oxide "XX." ¹

	First coat.	Second coat.	Third coat.
Zinc oxide.....	100 lbs.	100 lbs.	100 lbs.
Raw linseed oil.....	10 gal.	5½ gal.	6 gal.
Turpentine.....	½ gal.	1 gal.
Drier.....		½ gal.

359. Covering Tests. Each of these paints was applied over hard pine boards, soft pine boards, cedar clapboard siding, and white pine clapboard siding, the surface covered being approximately six and one-half square feet with each wood. The weights of paint applied were carefully determined and the following tables of figures were obtained by calculating back to the paste form, i.e., the form in which the goods were received in the original package, and in the case of white leads this represented the packages as found on the market. These calculations

¹ Bulletin No. 81, North Dakota Experiment Station.

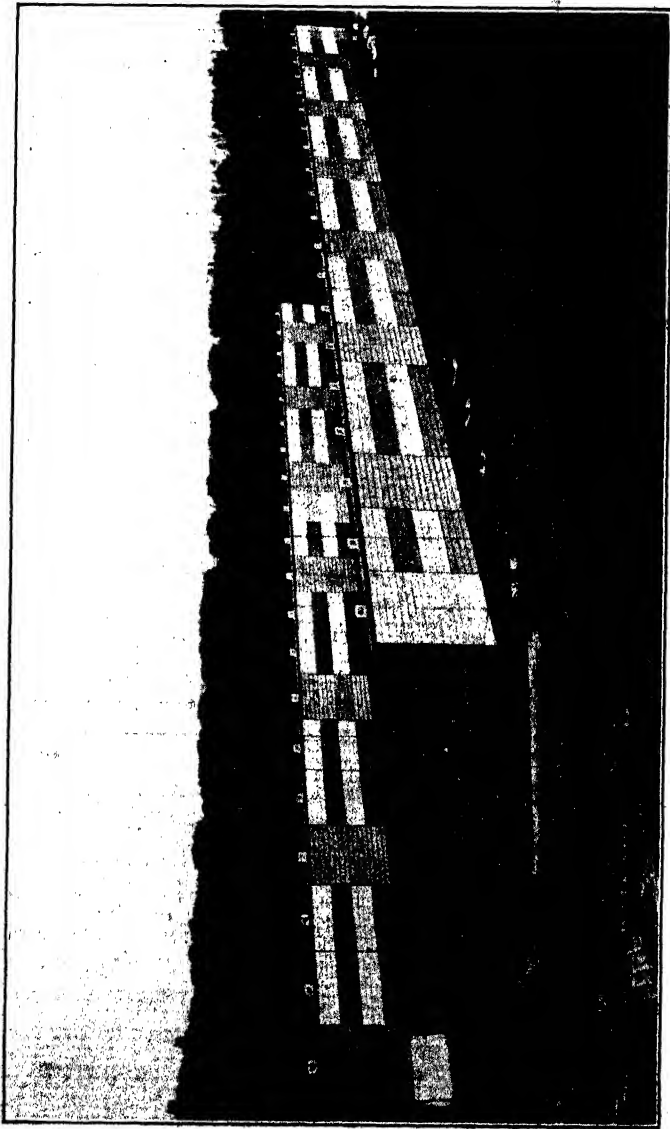


Fig. 77. — EXPOSURE FENCES. — NORTH DAKOTA. — EAST SIDE.

were prepared from the tables in Bulletin 81, North Dakota Experiment Station, and the author believes them to be measurably accurate. The Mild process tests were made at a later date, Mr. Campbell not being present. The conditions, however, were entirely similar, and the figures are from the official figures recorded at that time. The results are calculated in grams per 100 square feet. Not enough Matheson white lead was available for full sized tests and the amounts applied were not noted.

360. Hard Pine Boards, 100 Square Feet.

	First coat.	Second coat.	Third coat.	Total.
	Grams.	Grams.	Grams.	Grams.
Red seal.....	1330	863	725	2918
Eagle.....	1182	678	714	2574
Carter.....	1221	677	559	2457
Sublimed.....	1131	672	635	2438
Mild process No. 1 (double chased).....	1295	661	603	2459
Mild process No. 2 (mixed and ground).....	1146	688	668	2502
Zinc-lead white.....	1105	432	555	2092
Zinc oxide.....	702	531	432	1665

361. Soft Pine Boards, 100 Square Feet.

	First coat.	Second coat.	Third coat.	Total.
	Grams.	Grams.	Grams.	Grams.
Red seal.....	884	731	757	2372
Eagle.....	1084	610	573	2267
Carter.....	1038	645	767	2450
Sublimed.....	975	676	654	2305
Mild process No. 1 (double chased).....	931	598	520	2049
Mild process No. 2 (mixed and ground).....	918	621	619	2158
Zinc-lead white.....	1027	595	601	2223
Zinc oxide.....	662	474	391	1527

362. Cedar Clapboards, 100 Square Feet.

	First coat.	Second coat.	Third coat.	Total.
	Grams.	Grams.	Grams.	Grams.
Red seal.....	1361	974	815	3150
Eagle.....	1472	1027	808	3307
Carter.....	1152	777	750	2679
Sublimed.....	1208	852	644	2704
Mild process No. 1 (double chased).....	907	547	548	2002
Mild process No. 2 (mixed and ground).....	1005	601	636	2242
Zinc-lead white.....	1185	432	538	2155
Zinc oxide.....	924	481	462	1867

363. White Pine Clapboards, 100 Square Feet.

	First coat.	Second coat.	Third coat.	Total.
	Grams.	Grams.	Grams.	Grams.
Red seal.....	1288	594	577	2459
Eagle.....	1215	933	639	2787
Carter.....	1191	1045	719	2955
Sublimed.....	1275	750	704	2729
Mild process No. 1 (double chased).....	1301	763	782	2846
Mild process No. 2 (mixed and ground).....	1265	752	796	2813
Zinc-lead white.....	1168	641	449	2258
Zinc oxide.....	794	547	480	1811

364. Conclusion. In the opinion of those who conducted the tests there was no choice in the hiding power of any of the white leads after the third coat had been applied and dry enough to warrant inspection. The author leaves all conclusions to the reader, who if he may care to do so can easily calculate the area covered per 100 pounds, which is the more usual form of expression, or similarly calculate the total area covered per 100 pounds irrespective of the varieties of wood over which applied. It

is not the purpose of the author to advertise any particular brand or process, and the above figures are here given to show the variations in amounts applied, even with an exceedingly experienced and careful brush hand and under as like conditions as possible, and to act as a suggestion that it is unwise to state definite empirical figures from a single test.

CHAPTER XXIV.

THE ART OF GRINDING WHITE LEAD, PASTES, AND PAINTS.

365. Importance of Careful Grinding. This is essentially an age of competition, a fact which has become especially noticeable in the paint industry. Paint manufacturers have been accustomed to large profits, which are, however, rapidly becoming a thing of the past, and the manufacturer must accustom himself to a moderate return on his invested capital, and pay closer attention to the details of his business. The grinding of cheap combination white leads and selling them as pure white leads is not the profitable business it was formerly; the consuming public is getting wiser and more discriminating. Manufacturers whose specialty is cheap "dope" paints, or who in order to retain the odor of sanctity manufacture and sell them through a subsidiary corporation or company, are finding it harder and harder with each succeeding year to dispose of their wares. This means that paint manufacturers in order to hold their trade will have to use better materials. Many manufacturers have come to realize this and are so doing. Good materials, however, do not make good paint unless these materials are properly ground and incorporated. This requires time in the mixing and grinding, which involves a considerable item of expense in keeping the mills properly dressed.

366. Careless Grinding. Many manufacturers are very slow to recognize the importance of careful and fine grinding. The writer while a member of the staff of the North Dakota Experiment Station examined 54 paints consist-

ing of whites, colonial yellows, and grays which were supposed to have been prepared with especial care by the manufacturers, as they were used to demonstrate the wearing values of various pigments and formulas. After having stood under average conditions for 8 months they were examined in the can as to condition. Twelve, or 22 per cent, were coarse, giving evidence of very careless grinding; 15, or 28 per cent, gave evidence of hardening, also presumably due to lack of care in preparation or of observing suitable precautions in grinding. Fifty per cent only were in first-class condition. Yet these 54 paints came from the largest and most progressive houses, whose aggregate yearly sales would undoubtedly more than equal the combined sales of the remaining paint houses in the country.

367. Conditions to be Observed. The white lead or paint manufacturer, therefore, should give careful heed to the condition of his mills and the conditions under which they are operated. Cheap stones, careless or infrequent dressing, loose adjustment, hasty or careless mixing, will produce poor paint, no matter how good may be the material used. The heating of mills and the use of water-cooled mills have already been discussed in several places in this book and need not be taken up again in this connection.

368. Mixing and Chasing. Before being delivered to the grinding mills the pigments and linseed oil or other vehicles are incorporated either in a mixer or by means of a chaser and mixer. Chasing the pigments and oil first, then placing in a mixer, is undoubtedly far superior to mixing alone, although the writer is sorry to say that the latter practice is the one most commonly followed. Chasing brings the pigment particles in very close contact with each other and with the oil, and will effect a more thorough distribu-

tion of the different pigments present than is accomplished in an ordinary mixer. It is a well-known fact that a paint properly chased, mixed, and ground will occupy considerably less volume than a paint simply mixed and ground. In many instances when there is a rush of orders the mixing is done hastily and the "mix" let down into the mill before all of the pigment particles have come in contact with the oil and become thoroughly saturated; this increases the difficulty of grinding and increases the wear on the stones, as well as lessening the wearing value of the paint.

369. Proper Selection of Stones. Every practical paint grinder should be able to judge the different stones necessary for the grinding of various materials, — as, for instance, ores, which are sometimes ground into very fine particles in order to make the different paints, pastes, or pigments, — and furthermore learn to know the various reliable houses furnishing such stones. The author desires at this point to express his appreciation for the valuable information and drawings furnished in this connection by Paul Oehmig & Co., who have had a wide experience in the construction of mills.

370. Every millstone must feel sharp to the touch and possess a natural cut. Successful milling depends almost entirely upon proper judgment in selecting these stones, as only such stones as possess a natural cut can be successfully dressed, which is, of course, necessary for grinding the various materials.

371. Source of Millstones. The most valuable stone material is the so-called "Fresh Water Quartz," which is imbedded in the chalk deposits, particularly in France, and these are commonly called "Old Stock French Buhrs," and are adapted for all milling processes. Others of a denser grain are found near the mouths of former hot springs, and

still others are found in low marshy ground, which contained much vegetable matter at the time of their formation. The scientific name for the former is "Hydro-Quartzite," and for the latter "Limno-quartzite." The two latter kinds vary in structure and are usually called "New Stock French Buhrs." These are particularly fitted for the grinding of very hard minerals, and are generally used for this purpose, particularly in the preparation of paints, although the greater majority of these stones were, and are, imported from France, yet within the past twenty years there has been found on the American continent a considerable quantity of such stones which take the place of the imported ones, many of which, although not porous, are admirably suited for various milling purposes, and are sometimes preferable to the imported stones.

372. Domestic Stones. The domestic stones are composed of various sizes of quartz crystals and pebbles firmly united by a natural cement, and their hardness and natural "cut" suits the purpose, especially for grinding colors in oil, paste, paints, etc. The common name for these stones is "Esopus," or "Pebble Grit." The domestic stones on account of the proximity of the pebbles to each other often become glazed in grinding pastes and thereby lose their natural cut and in this respect are inferior to the imported French buhrs. However, for dry grinding, especially of medium-tempered minerals, the domestic varieties are considered preferable.

373. Stone Dressing. From the grooved mortars used by the ancient Egyptians 4000 years B.C., there developed the hand mills, which, as may be observed from old illustrations and excavated originals, consisted of a stone surface upon which the material was ground with a pestle, hollow stones or with wooden blocks. These later were developed into large circular stone mills, in which other than human

power was used, as early as 200 years B.C., as mentioned in various historical accounts, and in later years similar mills of various types formed a very important part of the equipment of the Roman Legions, particularly those of Cæsar, and their remains were found centuries afterwards on the Roman highways. Naturally the surfaces of these mills became worn smooth, and it was necessary to invent an artificial way of renewing the cutting surface, and therefore arose the system of grooving the stones, and thus improving and renewing the grinding surface. This dressing soon took on a definite character, and is found on many stones which are exhibited in museums, as, for instance, at Field's Museum at Chicago, Illinois. They were, however, less particular in their choice of material, choosing the most convenient, such as granite, sandstone, or lava.

374. In more recent times it has become necessary to use well constructed grinding mills in order to overcome the difficulties of grinding various minerals and paints. And to-day it is required that the mills must be easily adjustable and so constructed as to admit of easy access to the grinding stones.

375. Types of Mills. Under running mills, which by their greater pressure are more effective, are generally preferable to the over running mills. If the under stone is fixed, and the upper stone rotates, the material will very slowly be carried over the grinding surface of the bed stone until at length it reaches the circumference and falls out. On the other hand, if the understone is to be one that rotates, all particles lying on it will be hastened along by centrifugal force, the grinding surface of the upper stone asserting a pulverizing action on the larger particles, hindering their passage outward. Correctly arranged furrows further the movement of the material and it therefore follows that under runners are better forwarders and deliverers than

over runners, and there is less chance for accumulation and over heating.

376. Best Method of Dressing Stones. No definite system can be outlined which will be safe to follow in all cases. In the grinding of paints it is not so much a question of cutting surface as of pressure with which to reduce the material to the desired fineness. The grinding of cereals, on the other hand, necessitates a very fine, sharp and systematic dressing. The stones, in both cases, must possess a number of furrows, which bring the material from the center of the stones to the actual grinding surfaces where the material is actually ground. These furrows are necessary in order to avoid undue heating of the material, and in order to avoid overloading the grinding surface. In under running mills, these furrows should never be too deep on the running stone, but on the stationary stone they should be deeper. It is also necessary that the surface of the stones be a little concave, or tapered down to the eye, which adds to the efficiency of the grinding surface. By following out the above suggestions it will be found that the mill will always run cool and that it will be impossible to overload the grinding surface.

377. Adjustment of Grooves. Dressing was originally done in circular and radial grooves, but this was found not to be practical for every purpose, for the reason that when two corresponding grooves of the two stones come together, they should cross in such a way as to make a scissor-like movement, and never cross in two angles. Figures 78 and 79 designate the kinds of dressings which are most easily kept in order, and which are best for various purposes. These two dressings can only be recommended for dry grinding.

378. Grinding Pastes. A portion of Fig. 79 is designed to show the actual working of the two grinding surfaces, as

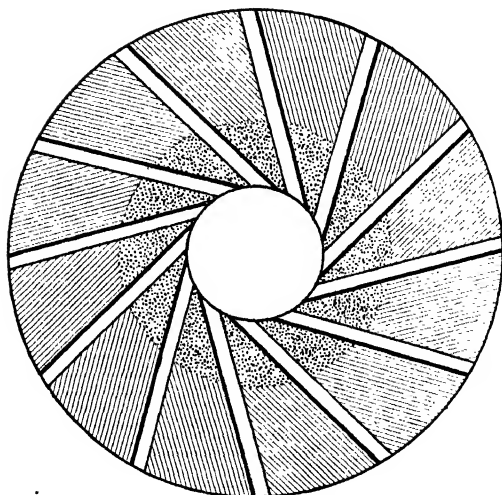


FIG. 78. — DRESSING FOR PAINT MILL.

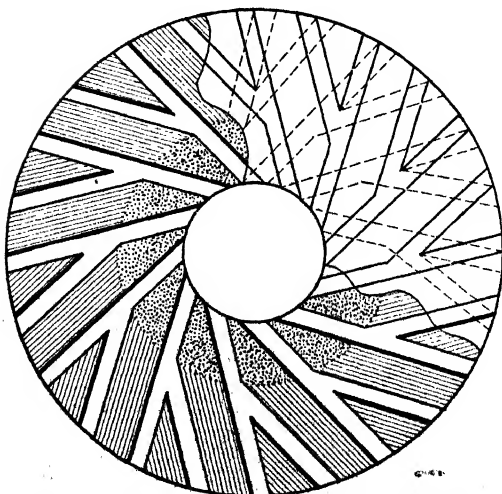


FIG. 79. — ADAPTION OF GRINDING SURFACES.

they should be, and at which angle and direction the two sets of grooves cross each other and what relation their direction has to the direction of the movement. The relation of the furrows is shown on Fig. 80. For the grinding of colors the following kinds of dressings should be used. Fig. 81 is an illustration of a French buhrstone of about thirty inches in diameter, which is practically efficient for grinding heavy pastes, colors, etc., which contain a large percentage of silicates. The furrows are quite wide and deep. The stones should be dressed three-eighths of an

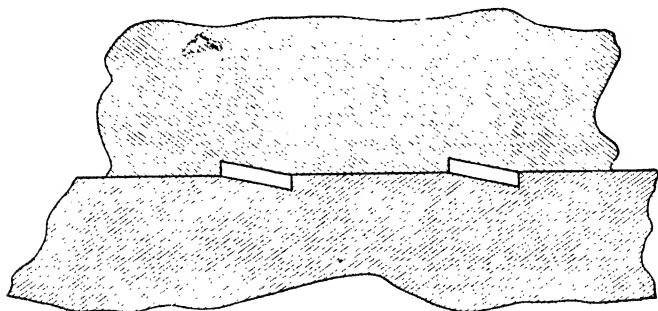


FIG. 80. — ADJUSTMENT OF FURROWS.

inch apart and the grinding face should not be over $7\frac{1}{2}$ to 8 inches. In order to facilitate the introduction of the material to be ground, it is preferable to deepen the furrows somewhat toward the center, as well as deepen the grinding surface toward the eye of the stone. For the grinding of oil colors and enamels a 20-inch mill with 4-inch face is generally used (see Fig. 82).

379. Use of Mill Picks. In dressing the stones, care should always be taken that the mill picks are not too heavy and are in proper shape on the cutting edge to avoid splintering and smashing the grinding surface of the stones. The furrows of the grinding stones should be cut

as smooth as possible, also it is preferable to have the furrows wide rather than cutting them in a ditchy-like appearance, as the furrows are the actual transmitters of the material to the grinding surface. If this style of dressing is followed the life of the millstone will be longer and a great deal of trouble and annoyance prevented.

It will be noted that Fig. 81 does not show the furrows cut to the edge of the stone, but it is the opinion of

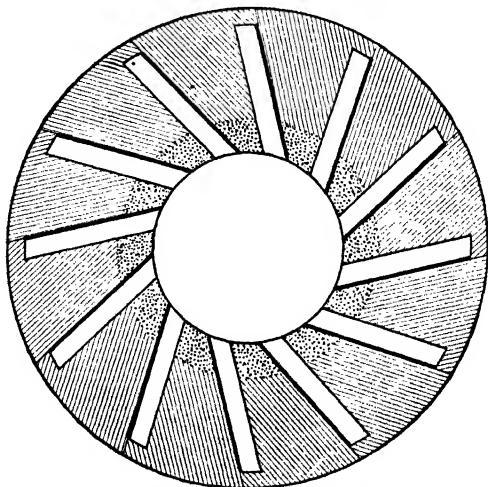


FIG. 81. — DRESSING FOR HEAVY GRINDING.

several stone manufacturers that it is best to cut these furrows to a feather edge up to the rim of the stone, but this should be the shop practice.

380. Pneumatic Dressing. The majority of the larger paint manufacturers now dress their mills with a pneumatic chisel, thereby saving considerable time and labor, but the writer has noticed that where the pneumatic tool is used there is a tendency toward careless dressing. This is probably due more than anything else to inefficient

workmen, as formerly mill dressing was a recognized trade, commanding good wages, and from long experience the men came to understand all of the fine points and requirements of the trade, but with the advent of the pneumatic tool the mills have been intrusted to the care of cheaper and less experienced workmen who have made little or no study of paint grinding.

381. Frequency of Dressing. The frequency with which mills should be dressed is a much debated question and

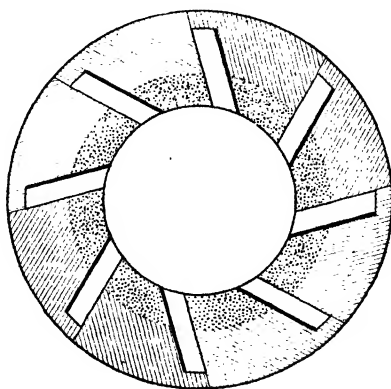


FIG. 82. — DRESSING FOR 20 INCH MILL.

depends to a large extent on the nature of the material to be ground and the tightness of the tension used. One of the leading manufacturers, whose lead and paste mills are in almost continuous operation, takes down his mills for dressing about once a year, varying as occasion may demand between six and eighteen months. The inevitable consequence was that the stones had, long before the time of dressing, worn smooth, the grooves having entirely disappeared, and in order to secure the customary output the tension had been released to such an extent that the stones exerted little if any grinding or crushing force on

the pigment particles. It is needless to add that his products plainly showed lack of grinding.

382. Paint grinders who have given the matter careful study dress their paste, semi-paste and lead mills every hundred to two hundred grinding hours, varying somewhat as occasion may require. Strictly pure leads which are of very fine texture are not as hard on the mill and consequently it may go for a considerably longer period. Much of course depends on the hardness and nature of the stones themselves. The above figures are based on an average grade of domestic stones. The various lead and zinc pigments are easy to grind as compared with ochres, metallics, e.g., Princes, and the various greens, etc.

383. Types of Dressing. As the dressing of mills is essentially the development of a scissor-like movement between the surfaces, the dressing of mills for the grinding of various paint products resolves itself into a fine dressing for oil color and coach color mills, which are usually about twenty inches in diameter, having a medium face and furrows of medium draft, while large mills for heavy pastes require a much heavier, deeper and sharper edged dressing with sufficient draft to move the product swiftly between the grinding faces to the edge. With a freshly dressed mill there is always a strong tendency of heating, which by expansion tightens the tension, increasing the friction and thus making the heating more rapid. Especial attention should be given a freshly dressed mill and the tension released as the mill begins to warm up. It is almost unnecessary to state that all mills should be as efficiently water cooled as possible.

384. Speed of Mills. As in the above instance no definite rules can be laid down. Some factories are running their mills at a rate of from 55 to 60 r.p.m. with very satisfactory results, while others do not run over 35 to 40 r.p.m., as it

largely depends upon how the product to be ground is treated before it is given to the mill, also upon the nature of the product, and upon the construction of the mills used for grinding same. Mills grinding very heavy pastes should run slower, 35 to 40 r.p.m., while mills grinding an easy-to-finish or liquid paint, can run faster, 50 to 60 r.p.m.

CHAPTER XXV.

ANALYSIS OF COMMERCIALY PURE WHITE LEADS.

385. Sulphur Dioxide. In the manufacture of quick process white leads, where the carbon dioxide is obtained from fuel gases, it is liable to contain sulphur compounds which will remain in the white lead combined in the form of sulphite of lead.

386. The sulphur dioxide may be estimated by treating 10 grams of the pigment with 50 c.c. of water and 25 c.c. of hydrochloric acid. Allow to stand 5 minutes and titrate with hundredth normal iodine solution as described under the estimation of sulphur dioxide in zinc pigments. The same objections apply to its presence in white lead as in zinc oxides.

387. Sandy Lead.¹ "A certain degree of density is always desired in white lead, since both the corroder and the grinder know that the smaller the amount of oil required to bring a given lead to paste form, the cheaper it is for him, since the average price per pound of linseed oil is greater than that of dry lead, while the same pigment is equally sought after by the consumer, since he, too, desires density and opacity in this pigment. However, efforts in this direction are not infrequently carried too far, with the result of a crystalline overcorroded lead, which settles and hardens badly. Such lead causes loss and trouble both to the grinder and the consumer.

388. Determination. "Based upon the undesirable feature of settling, a comparative separation is easily made.

¹ Hooker, Treatise on White Lead, page 24.

A fairly large sample, say 100 grams, is taken. This if in paste form is thinned with benzine and run through a fine bolting cloth. Any paint skins are retained, but all of the lead should, when sufficiently thinned, wash through a fine bolting cloth. The very thin paint is now thoroughly stirred and allowed to settle for a short time only. Nearly all of the benzine is now poured off and then the washing of the sediment with benzine repeated until the benzine comes off nearly clear, leaving the 'sand' alone as a residue." While present in all commercial lead, the amount should be small, scarcely exceeding 2.5 per cent; objectionable samples will frequently show much more, at times over 10 per cent.

389. Tan-bark. The determination of tan-bark and other organic matter is seldom required. It may, however, be made by dissolving 50 grams of the sample in 75 c.c. of nitric acid diluted with 250 c.c. of water. Filter through a weighed Gooch crucible, provided with a disk of filter paper on the top of the asbestos felt, wash thoroughly dry and weigh. The amount present should not exceed one-tenth of one per cent, according to Hooker.

390. Sulphate of lead, which may be present in some of the quick-process leads, would largely remain undissolved in the nitric acid solution and unless removed would be weighed up as tan-bark, etc. When present it may be dissolved by placing the Gooch crucible and contents in a small beaker containing acid ammonium acetate for a few minutes, after which the crucible is placed in the holder, washed with a further quantity of acetate solution, then with a little warm water, and dried as before.

391. Metallic Lead. Like the previous determination it is seldom made. Occasionally in poorly prepared white leads a sufficient amount may be present to warrant a determination; in which case it is best made in conjunction

with the determination of "sandy lead," which, after being weighed up, is carefully dissolved in dilute nitric acid, the operation being checked the moment the sandy white lead has dissolved by dilution with a large quantity of water. The particles of metallic lead are but very slightly acted upon by acid and may be filtered off on to a weighed Gooch crucible, washed thoroughly, dried and weighed. The amount found should not exceed one-tenth of one per cent.

392. Lead Sulphate. This impurity may be present in small quantities in white leads prepared by the newer processes and sometimes in old Dutch process lead in the settling tanks and wash water tanks. When present in quantities less than one-half of one per cent it should not be considered as seriously objectionable.

393. Determination. Dissolve 1 gram in water 25 c.c., ammonia 10 c.c., hydrochloric acid in slight excess.

Dilute to 200 c.c., and add a piece of aluminum foil which should about cover the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, boil until the bromine is expelled, add 15 c.c. of barium chloride, boil 10 minutes, filter, wash with hot water, ignite and weigh as barium sulphate. Calculate to lead sulphate by multiplying by 1.3 as a factor.

394. Volumetric Estimation of Lead, Method I.¹ Dissolve 1 gram in 15 c.c. nitric acid, specific gravity 1.20, neutralize the solution with ammonia in excess, and then make strongly acid with acetic acid. It is then boiled and

¹ Wainwright, J., Am. Chem. Soc., vol. 19, page 389.

standard potassium bichromate solution in sufficient quantity to precipitate nearly all the lead is run in from a burette. The liquid is boiled until the precipitate becomes orange colored. The titration is continued, one-half c.c. or so at a time, the solution being well stirred after each addition of bichromate until the reaction is almost complete, which can be observed by the sudden clearing up of the solution, the lead chromate settling promptly to the bottom of the beaker; this will usually occur within 1 c.c. of the end of the reaction. The titration is then finished, the end point being indicated by the use of a silver nitrate as an outside indicator, on a white plate.

The solution of the lead salt should be as concentrated as possible before titration and decidedly acid with acetic acid. The titration should be performed in a solution kept at all times as near the boiling point as possible.

395. Potassium Bichromate Solution. This should be of such strength that 1 c.c. equals approximately 0.01 gram of metallic lead, and should be standardized against a weighed amount of pure metallic lead as described above.

396. Silver Nitrate Solution. Dissolve 2.5 grams of silver nitrate in 100 c.c. of water.

NOTE.— This method is applicable for determination of lead in red lead, the solution being effected with nitric acid, boiling, and adding dilute oxalic acid drop by drop until the lead oxide formed is completely dissolved.

397. Volumetric Estimation of Lead, Method II.¹ Dissolve 0.5 to 1 gram of the pigment in acetic acid if white lead, if lead sulphide, dissolve in nitric acid, dilute with 25 c.c. cold water, add strong ammonia until just alkaline to litmus paper, then make distinctly acid with strong acetic acid.

¹ Alexander's Method, Ore Analysis, Low, page 113.

398. Heat to boiling, dilute to about 200 c.c. with boiling hot water, and titrate with standard ammonium molybdate solution. Reserve about 10 c.c. of the hot solution in a small beaker, run in molybdate solution into the large beaker from a burette, with constant stirring, until a drop placed in contact with a drop of tannic acid solution on a white plate gives a brown or yellow tinge. Add the 10 c.c. reserved and finish the titration carefully at the rate of two drops addition at a time. When the final yellow tinge is obtained, it is probable that some of the immediately preceding test drops may have developed a tinge also. If such is the case deduct the volume of two drops from each test showing a color from the final burette reading.

399. Molybdate Solution. Prepare a solution of ammonium molybdate 1 c.c. of which is equal to approximately .01 gram of lead. Standardize against a weighed amount of chemically pure lead, dissolving in nitric acid and treating as described above.

400. Tannic Acid Solution. Dissolve 0.5 gram of tannic acid in 100 c.c. water.

401. Carbon Dioxide. The amount of carbon dioxide in white lead can be most accurately estimated by means of Knorr's apparatus.

This apparatus employs only ground-glass joints, and may be quickly made ready for use or taken to pieces and packed away. On the other hand, it is inflexible and must be carefully handled. *A* is distilling flask fitted to condenser by a ground-glass stopper; *B*, reservoir containing acid; *C*, soda-lime tube; *D*, condenser; *E*, calcium chloride tube; *F*, U-tube filled with pumice stone moistened with sulphuric acid, followed by a calcium-chloride tube *G*. The three soda-lime tubes *H*, *H*, *H* are followed by a calcium chloride tube *K*, which is connected with an aspirator at *L*.

The calcium chloride and soda lime employed should be finely granulated and freed from dust with a sieve.

402. One gram of the sample to be examined is placed in the distilling flask, which must be perfectly dry. The flask is closed with a stopper carrying the tube connecting with the absorption apparatus and also with the funnel tube. The tubes in which the carbon dioxide is to be absorbed are weighed and attached to the apparatus. In case two Liebig bulbs are employed, one for potassium hydroxide and the other for sulphuric acid, to absorb the moisture given up by the potassium hydroxide solution, it

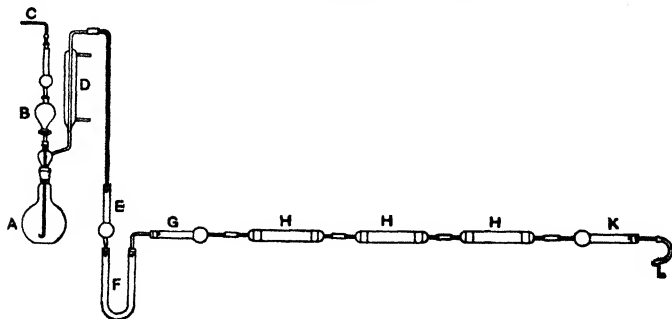


FIG. 83. — KNORR'S APPARATUS.

will be necessary to weigh them separately. If soda-lime tubes are employed it will be found advantageous to weigh them separately and fill the first tube anew when the second tube begins to increase in weight materially. The bulb *B* is nearly filled with hydrochloric acid (sp. gr. 1.1), and the guard tube *C* placed in position. The aspirator is now started at such a rate that the air passes through the Liebig bulbs at the rate of about two bubbles per second. The stopper of the funnel tube is opened and the acid allowed to run slowly into the flask, care being taken that the evolution of the gas shall be so gradual as not to materially increase the current through the Liebig bulb.

403. After the acid has all been introduced, the aspiration is continued, when the contents of the flask are gradually heated to boiling, the valve in tube *B* being closed. While the flask is being heated the aspirator tube may be removed, although many analysts prefer when using ground-glass joints to aspirate during the entire operation. The boiling is continued for a few minutes after the water has begun to condense in *D*, when the flame is removed, the valve in the tube *B* opened, and the apparatus allowed to cool with continued aspiration. The absorption tubes are then removed and weighed, the increase in weight being due to carbon dioxide.

404. Where extreme accuracy is desired the carbon dioxide after passing through the condenser should pass through a U-tube filled with calcium chloride, a U-tube filled with lumps of dehydrated copper sulphate moistened with sulphuric acid (sp. gr. 1.84), and then through a U-tube filled with pumice stone moistened with sulphuric acid before being absorbed by soda-lime. The air used for aspirating should also pass through a large U-tube filled with soda lime before passing through the small soda-lime tube *C*. In order to make the apparatus compact the soda-lime tubes may be laid side by side on a small rack constructed for the purpose, the soda-lime tubes being connected with each other by small U-shaped glass tubing connections.

405. **Acetic Acid in White Lead.**¹ "In the manufacture of white lead by any process involving the use of acetic acid, a certain portion of the acetic acid seems to be bound firmly so that it cannot be washed out in any ordinary process of manufacture. The amount of the acetic acid which is fixed by the white lead depends largely upon the quantity used in the process of manufacture. The Navy Yard specifications demand a white lead which shall not

¹ G. W. Thompson, *J. Soc. Chem. Ind.*, vol. xxiv, No. 9.

contain 'acetate in excess of fifteen one-hundredths of 1 per cent of glacial acetic acid.' It seems reasonable, furthermore, that whether the acetic acid is objectionable or not, the intelligent purchaser of white lead should be enabled, as far as possible, to know what he is buying, and perhaps trace back results to some definite cause.

406. "Ordinary lead acetate solution will take up varying amounts of lead oxide to form basic lead acetate. The more concentrated the lead acetate solution is, the less basic will be the formed acetate; for instance, the ordinary pharmacopœia solution — 'Liquor Plumbi Subacetatis' — contains two equivalents of lead to one of acetic acid, and, while this solution may be made more basic than this by adding an excess of litharge, the amount of litharge which it will take into solution in excess of that required to form the pharmacopœia solution is comparatively small."

407. "Working with dilute solutions of lead acetate, however, solutions can be obtained containing as much as ten equivalents of lead to one of acetic acid. These very basic dilute solutions may, however, be regarded by some as supersaturated solutions, for the reason that the basic lead tends to separate out on slight provocation, carrying with it some acetic acid. If this very basic lead acetate, which separates out, is washed with distilled water, it appears to form a colloidal solution, from which the basic lead is readily precipitated in the presence of suspended inert material, and especially in the presence of electrolytes. Ordinary water is usually used for washing white lead, and, as this water contains more or less saline substances, any of this extremely basic acetate that is present will be precipitated with the white lead, and go into the ~~finished product.~~"

408. "Determination. 18 grams of the dry white lead are placed in a 500-c.c. flask, this flask being arranged for con-

nection with a steam supply, and also with an ordinary Liebig condenser. To this white lead is added 40 c.c. of syrupy phosphoric acid, 18 grams of zinc dust, and about 50 c.c. of water. The flask containing the material is heated directly and distilled down to a small bulk. Then the steam is passed into the flask until it becomes about half full of condensed water, when the steam is shut off and the original flask heated directly and distilled down to the same small bulk, this operation being conducted twice. The distillate is then transferred to a special flask and 1 c.c. of syrupy phosphoric acid added to insure a slightly acid condition."

409. "The flask is then heated and distilled down to a small bulk — say, 20 c.c. Steam is then passed through the flask until it contains about 200 c.c. of condensed water, when the steam is shut off and the flask heated directly. These operations of direct distillation and steam distillation are conducted until 10 c.c. of the distillate require but a drop of N/10 alkali to produce a change in the presence of phenolphthalein. Then the bulk of the distillate is titrated with N/10 sodium hydroxide, and the acetic acid calculated. It will be found very convenient in this titration, which amounts in some cases to 600 to 700 c.c., to titrate the distillate when it reaches 200 c.c., and so continue titrating every 200 c.c. as it distills over."

410. "Conclusions. The details in this described method, as regards the supply of steam from an outside flask, its condensation and subsequent evaporation, are not essential to the process, but can, of course, be modified so as to conform to the ordinary method of distilling acetic acid from acetate of lime. If the white lead contains appreciable amounts of chlorine, it is well to add some silver phosphate to the second distillation flask, and not to carry the distillation from this flask too far at any time. If the dry

white lead under examination has been obtained by extraction as a residue from white lead paste, it is well that this extraction should be exceedingly thorough, as otherwise fatty acids may be held and distilled with the acetic acid. Even then they will not interfere with the final titration, as they may be filtered from the distillate before titration, should that be desired."

CHAPTER XXVI.

ANALYSIS OF THE ZINC PIGMENTS.

411. Moisture. Two grams of the pigment are weighed out on to a watch glass, provided with a cover glass and clip, dried for two hours in a steam oven, the cover glass placed in position and held by the clip, the glasses cooled in the desiccator and weighed. Loss in weight represents the amount of moisture in the pigment.

412. Silica. Weigh one gram of pigment into a 250-c.c. covered beaker, add 25 c.c. of concentrated hydrochloric acid, heat gently for five minutes, or until the pigment has dissolved (if lead sulphate is present in considerable quantity, this may take quite a few minutes), add 50 c.c. hot water, and continue the heating for about five minutes longer. Filter boiling hot with the aid of suction, washing thoroughly with boiling water so as to thoroughly remove all the lead and zinc salts from the filter-paper. The filter-paper and any residue of silica is burned, ignited and weighed in the usual manner. Any weighable residue is reported as silica.

413. This treatment may give results that are slightly low, owing to the slight solubility of silica in strong hydrochloric acid, but for commercial purposes this slight error may be neglected. In carefully prepared zinc pigments the amount of silica present will be unweighable; even with careless processing the amount will seldom exceed a very few hundredths of one per cent.

414. Sulphur Dioxide. Weigh 3 grams of ~~the pigment~~ into a 250-c.c. beaker; add 100 c.c. of distilled water, that has been *recently boiled* and cooled. Add 5 c.c. of concen-

trated sulphuric acid, stir thoroughly and allow to stand 15 minutes. Titrate with standard hundredth normal iodine solution, using starch paste as an indicator.

1 c.c. hundredth normal iodine = 0.00032 gram sulphur dioxide.

415. Preparation of Reagents — Iodine Solution. Dissolve 1.268 grams of pure iodine and 1.8 grams of potassium iodide in about 150 c.c. of water in a graduated liter flask. After solution, fill to the mark with water that has been freshly boiled.

416. Sodium Thiosulphate. Dissolve 2.5 grams in recently boiled distilled water and make up to one liter. Preserve in a brown glass bottle or one that has received a liberal coat of asphaltum.

417. Starch Paste. One gram of starch is boiled in 200 c.c. of distilled water.

418. Standardizing the Sodium Thiosulphate Solution. Pipette 20 c.c. of standard potassium dichromate solution in a 250-c.c. beaker; add 10 c.c. of a 15-per cent solution of potassium iodide. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of thiosulphate to run in slowly from a burette until the yellow color has almost disappeared. Add a few drops of starch paste and continue the addition of thiosulphate with constant stirring until the blue color just disappears. The burette reading is then made and the value of the thiosulphate calculated.

419. Standard of Acceptance. A good grade of zinc oxide should contain only a trace of sulphur dioxide. Many paint chemists reject oxides containing more than six hundredths of one per cent. The reason for this is that the sulphur dioxide affects the character of the linseed oil very strongly, causing the paint to thicken and ultimately "liver" in the package. This may be shown in an experimental way by dividing a sample of zinc oxide into

two parts, exposing one part to an atmosphere of sulphur dioxide, then spreading equal amounts of both samples on a glass plate and mixing to a paste with the same number of drops of oil in exactly the same manner. It will be found that the sample containing the sulphur dioxide will be thicker and stiffer than the other, showing the effect of the sulphur dioxide on the oil.

420. Reaction with Rosin Products. In the presence of rosin products of any kind, such as are often used in the driers of mixed paints, sulphur dioxide acts as a contact agent of great strength, causing changes all out of proportion to the amount present, often resulting in hardening, "washing" of the paint film, "livering" in the package, etc. These results will be influenced to a considerable degree by the acidity, moisture, and temperature of the paint, and hence no hard and fast deductions can be made as to what may be expected of any particular paint containing sulphur dioxide in excess of the prescribed amount.

421. Zinc Sulphate. Ten grams of the pigment are weighed into a 250-c.c. Erlenmeyer flask, 100 c.c. of boiling water added. The contents of the flask are then shaken thoroughly for several minutes and filtered and the residue on the filter paper washed with several portions of boiling water. The soluble zinc in the filtrate is then titrated as described under the Estimation of Zinc by titration with ferrocyanide, and calculated to zinc sulphate.

422. It is not advisable to boil the zinc oxide pigment with the water, as interaction may occur between the zinc oxide and any lead sulphate present, resulting in the formation of more zinc sulphate. Neither is it wise to estimate the soluble combined sulphuric acid in the hot aqueous filtrate and calculate to zinc sulphate, as there often seems to be an excess over what is required to form

the normal sulphate of zinc and hence the results are apt to be too high.

423. Effect. Zinc sulphate is not considered by many paint chemists to be as objectionable in zinc pigments as sulphur dioxide, and is often permitted in amounts under one per cent. In amounts above one per cent it seems to act as an astringent on the oil when used in the preparation of mixed paints, tending to prevent the proper penetration of the wood, especially if the paint has been ground for some length of time. A prominent paint chemist discusses its effect as follows: "The action of zinc sulphate is two-fold: first, as an astringent upon the oil and tending to cause a distinct demarcation between two coats; and second, that of a contact agent, facilitating reaction between the different pigments. The visible results of its presence are peeling and 'washing.' Apparently, rather more than the normal amount of moisture must be present to cause its activity, and if the paint coat has set under dry or normal conditions, the zinc sulphate produces no apparent effect." In the exposure tests conducted by the author, the worst cases of "washing" have occurred with zinc pigments in which the sulphur dioxide was less than one one-hundredth of a per cent and the zinc sulphate between one and one and one-half per cent.

424. Lead. The lead present in zinc pigments is usually in the form of sulphate and may be estimated by either of the following methods.

425. Method I. The filtrate from the silica, which need not exceed 100 c.c. in volume if the washing has been judiciously conducted by suction or the hydrochloric acid solution, if silica is absent, is evaporated very nearly to dryness in an uncovered beaker on the hot plate, avoiding actual boiling, 10 c.c. of warm water added and evaporated again nearly to dryness in order to expel the hydro-

chloric acid. Cool, add 30 c.c. dilute sulphuric acid, heat to boiling for five minutes in covered beaker, cool, add 50 c.c. of alcohol and allow to stand one-half hour or until all of the lead sulphate is precipitated from solution. Filter through a weighed Gooch crucible, washing thoroughly with 50 per cent alcohol, until the precipitate is entirely freed from zinc sulphate. Dry on hot plate, heat gently over a Bunsen burner, cool in desiccator, and weigh as lead sulphate. If heated over the flame before drying, a portion of the lead is liable to be reduced to lead oxide by the alcohol, and the weight will be low.

426. Method II. The lead may be separated from the zinc in a solution barely acid with hydrochloric acid, by hydrogen sulphide, the precipitated lead sulphide dissolved in nitric acid and titrated with standard molybdate or bichromate solution as described in Chapter XXX, Analysis of Combination White Leads, and White Paints.

427. Method III. The amount of lead sulphate may be rapidly estimated by dissolving a weighed amount of the pigment in dilute acetic acid, filtering on to a weighed Gooch crucible, washing with warm water, heating gently, and weighing the lead sulphate direct. Lead sulphate being slightly soluble in acetic acid the results will be somewhat low and can only be considered as roughly approximate.

428. Total Zinc. The zinc can be rapidly and accurately estimated volumetrically by the following methods.

429. I. Potassium Ferrocyanide Method. — Preparation of reagents.

430. Standard Zinc Solution. Dissolve 10 grams of chemically pure zinc in hydrochloric acid in a graduated liter flask, add 50 grams of ammonium chloride and make up to one liter.

1 c.c. = 0.01 gram zinc or 0.01245 gram zinc oxide.

431. Standard Potassium Ferrocyanide Solution. Dissolve 46 to 48 grams of crystallized potassium ferrocyanide in water, make up to 1000 c.c.

432. Uranium Nitrate Solution. Dissolve 15 grams of uranium nitrate in 100 c.c. of water.

433. Standardizing the Ferrocyanide Solution. To determine the value of the potassium-ferrocyanide solution, pipette 25 c.c. of the zinc solution into a 400 c.c., beaker. Dilute somewhat and make faintly alkaline with ammonia, bring to a faintly acid condition with hydrochloric acid and then add 3 c.c. excess of the concentrated acid, dilute to a total volume of about 250 c.c., heat to 80° C. and titrate as follows: Pour off about 10 c.c. of the zinc solution into a small beaker and set aside, run the ferrocyanide into the remainder from a burette, a few c.c. at a time, until the solution takes on a slight ash gray color, or until a drop of the solution placed in contact with a drop of the uranium nitrate solution on a porcelain plate turns to a distinct brownish color.

434. Often the end point has been passed by quite a little. The 10 c.c. of zinc solution that has been reserved is now added and the titration continued, drop by drop, testing a drop of the solution carefully on the porcelain plate after each addition of ferrocyanide solution. Some little time is required for the test drop to change color, so that the end point may have been passed slightly; this may be corrected for by making a memorandum of the burette readings, having the test drops arranged in regular order and taking as the proper reading the one first showing a distinct brownish tinge. Having noted the number of cubic centimeters ferrocyanide required for the titration of the standard zinc solution, the value of 1 c.c. may be readily calculated.

435. Titration of Sample. One-half gram of the sample if high in zinc, or 1 gram if the zinc content is fairly low, is dissolved in a covered beaker in 10 c.c. of hydrochloric acid and 10 c.c. of water, the solution diluted somewhat, neutralized with ammonia and treated exactly as described above for the standard zinc solution, care being taken to titrate to exactly the same depth of color on the porcelain test plate. If the method is carefully carried out, the procedure being uniformly the same in each determination, the results will be found satisfactorily accurate.

436. II. Precipitation of Zinc as Carbonate. The alcoholic filtrate from the lead sulphate method of estimating lead is heated gently until practically all of the alcohol has been driven off. The remaining liquid is transferred to a porcelain dish provided with a beaker cover, and sodium carbonate added cautiously until the liquid is alkaline, care being taken that no loss occurs due to the effervescence. The zinc is precipitated as a basic carbonate, and the solution should be boiled gently for a few minutes in order to insure complete precipitation. As stated above this operation should be conducted in a porcelain dish, as the boiling alkaline solution attacks glass to a considerable extent. Allow the precipitate to subside, decant through a filter, and boil the precipitate three times with water, decanting each time, wash thoroughly with boiling water, dry and remove the precipitate as completely as possible from the filter paper. Saturate the paper with a strong solution of ammonium nitrate, dry again and ignite the paper. The ammonium nitrate serves to oxidize any of the zinc that is reduced to the metallic state by the carbon of the filter paper and which would otherwise be lost by volatilization. The precipitate is then introduced into the crucible and converted by ignition into the oxide and weighed as such.

437. III. Precipitation of the Zinc as Phosphate. The alcoholic filtrate from the lead sulphate after the removal of the alcohol as described above is diluted somewhat if necessary, about 20 to 30 grams of dry ammonium chloride added and made alkaline with ammonia, then just *barely* acid with acetic acid and 10 c.c. of a cold saturated solution of microcosmic salt added. The solution is diluted to a bulk of about 200 c.c., heated nearly to boiling with vigorous stirring, in order to make the precipitate crystalline. Cool, make exactly neutral with ammonia, allow to stand until the precipitation is complete, filter on to a weighed Gooch crucible, washing with ammonium nitrate solution, ignite, and weigh as zinc pyrophosphate.

438. Combined Sulphuric Acid. Dissolve 0.5 gram to 1 gram of the pigment, according to the amount of sulphates present, in

Water, 25 c.c.

Ammonia, 10 c.c.

Hydrochloric acid, a slight excess.

439. Dilute to 200 c.c. and add a disk of aluminum foil, which should about cover the bottom of the beaker. Boil gently until the lead is precipitated, holding the disk if necessary to the bottom of the beaker with a glass rod. The completion of precipitation is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake and washing thoroughly to free from solution.

440. Add to the filtrate a few drops of bromine water, boil and precipitate with barium chloride in the usual manner for sulphates. In order to avoid a possible reduction of a portion of the barium sulphate in the pores of the filter paper during its incineration, the precipitate may be filtered directly on to a Gooch crucible, which after being

weighed has a disk of ashless filter paper placed on top of the customary asbestos felt. This will effectually prevent any of the precipitate from burrowing through the filter. The ignition of the precipitate in the presence of the small disk of filter paper will cause no appreciable reduction to sulphide.

441. Calculations. The amount of zinc present as sulphate of zinc is deducted from the total zinc and the remainder calculated to zinc oxide. The sulphuric acid combined with the zinc is deducted from the total combined sulphuric acid and the remainder calculated to lead sulphate. Any excess of lead over that required to combine with the sulphuric acid is calculated to lead oxide. Unless sublimed lead is present there will be little or no lead oxide.

442. Estimation of Arsenic and Antimony in Zinc Leads. Weigh 2 grams of the sample into a 200-c.c. digestion flask. Add 7 grams of potassium bisulphate, 0.5 gram of tartaric acid, and 10 c.c. of concentrated sulphuric acid. Digest carefully at first, but finally with the full power of a Bunsen burner until a clear mass remains, containing but little free sulphuric acid. Cool, spreading the melt around on the sides of the flask. Add 50 c.c. of water, 10 c.c. of strong hydrochloric acid, and digest for about twenty minutes without boiling.

443. Cool thoroughly under the tap, and filter off the separated lead sulphate. Dilute the filtrate to about 300 c.c. with hot water, maintain the liquid warm, and pass in hydrogen sulphide for about fifteen minutes or until precipitation is complete. Filter, washing with hydrogen sulphide water. Digest filter and contents in a rather small amount of yellow ammonium sulphide. Filter on suction cone, washing with as small a quantity of water as possible.

444. Digest the filtrate with 3 grams of potassium bisulphate and 10 c.c. of strong sulphuric acid over a free flame until all of the free sulphur and the larger portion of free acid are expelled. Cool, spreading the melt around on the sides of the flask as before. Add 25 c.c. of water and 10 c.c. of strong hydrochloric acid, and warm to effect complete solution. Cool under the tap, add 40 c.c. of strong hydrochloric acid, and pass in hydrogen sulphide until complete precipitation of the arsenic takes place, 15 to 30 minutes. The antimony remains in solution.

445. Filter off the precipitated arsenious sulphide on to a weighed Gooch crucible, washing with a mixture of two volumes of hydrochloric acid and one of water. The filtrate is reserved at this point for the estimation of antimony. The precipitate is next washed with alcohol, the crucible and contents placed in a small beaker, the crucible nearly filled with carbon bisulphide, and the contents allowed to digest at ordinary temperature for about twenty minutes in order to dissolve the free sulphur. The carbon bisulphide is removed by suction, the crucible dried in the steam oven, cooled, and the precipitate weighed as arsenious sulphide and calculated to arsenious oxide.

Weight arsenious sulphide $\times 0.8043 =$ weight arsenious oxide.

446. Instead of weighing as the sulphide, the arsenic may be estimated volumetrically as follows: Wash out the hydrochloric acid from the sulphide precipitate with hydrogen sulphide water. Digest filter and contents in a little warm ammonium sulphide, filter on a suction cone, wash with a little dilute ammonium sulphide solution. Place the filtrate in digestion flask, add 2 to 3 grams of potassium bisulphate and 5 c.c. of strong sulphuric acid. Evaporate, boiling to a small bulk, and then manipulate

the flask over a free flame until the sulphur is entirely expelled and most of the free acid also. Take up, after cooling, by warming with 50 c.c. of water, and then boil sufficiently to expel any possible sulphur dioxide. Now drop in a bit of litmus paper as an indicator, and then add ammonia until the solution is slightly alkaline. Again slightly acidify with hydrochloric acid and cool to room temperature. Finally, add 3 to 4 grams of sodium acid carbonate and a little starch liquor and titrate with standard iodine solution. Pay no attention to a slight discoloration toward the end, but proceed slowly until a single drop of the iodine produces a strong permanent blue color.

447. Preparation of Iodine Solution. The iodine solution may be prepared by dissolving about 11 grams of iodine in a little water with the addition of about 20 grams of potassium iodide and diluting to 1 liter. Standardize with arsenious oxide. Dissolve about 0.150 gram in 5 c.c. of strong hydrochloric acid by warming very gently, dilute and neutralize as described above, and finally titrate with the iodine solution. One c.c. of the latter will equal about 0.003 gram of arsenic.

448. Antimony. Very nearly neutralize the filtrate reserved for the antimony estimation with hydrochloric acid, dilute with double its volume of hot water, and pass in hydrogen sulphide until all of the antimony is precipitated. Filter, washing with hydrogen sulphide water. Digest filter and contents in a little ammonium sulphide, filter on suction cone and wash with dilute ammonium sulphide. Place the filtrate in the digestion flask and add about 3 to 4 grams of (pure) potassium bisulphate and 10 c.c. of strong sulphuric acid. Boil as previously described to expel first the water, then all the free sulphur, and finally most of the free acid.

449. Cool, add 50 c.c. of water and 10 c.c. of strong hydrochloric acid. Heat to effect solution, and then boil for a few minutes to expel any possible sulphur dioxide. Finally, add 10 c.c. more of strong hydrochloric acid, cool under the tap, dilute to about 200 c.c. with cold water and titrate with a standard solution of potassium permanganate. The solution ordinarily used for iron titrations will answer. The oxalic acid value of the permanganate multiplied by 0.9532 will give the antimony value.

450. Methods of Determining Small Amounts of Arsenic and Antimony in Use at Canon City, Colorado.

451. Method I. Take two or three grams of pigment and dissolve in 10 c.c. nitric acid and 10 c.c. sulphuric acid. Heat to expel the nitric acid and evaporate to sulphuric fumes. The advantage of the nitric acid is to oxidize the arsenic present and thereby avoid any loss of arsenious acid by volatilization. Allow to cool and dilute with cold water, add about 50 per cent of the volume of alcohol to insure complete precipitation of all lead as lead sulphate. Filter and wash, boil filtrate to expel alcohol, and add about ten to fifteen cubic centimeters hydrochloric acid. Precipitate the warm solution with hydrogen sulphide. Filter and wash with dilute hydrogen sulphide water. All arsenic, antimony, and copper are on the filter as sulphides. Test filtrate with hydrogen sulphide as a check on precipitation.

452. Dissolve the sulphides in caustic potash solution, then bring to a boil and pass hydrogen sulphide into warm solution as before. Filter and test filtrate. Wash with dilute ammonium sulphide solution. All arsenic and antimony are in filtrate and any copper present is on the filter. If any copper is present, dissolve and titrate by the iodide method.

453. Make filtrate acid with hydrochloric acid and add about 10 c.c. excess and pass in hydrogen sulphide gas as

before. Filter off the sulphides of arsenic and antimony and wash with hydrogen sulphide water. Dissolve these sulphides in about 10 c.c. aqua-regia, then dilute with water and make alkaline with ammonia, adding about 25 c.c. excess. Then add from one to two grams tartaric acid and 10 to 15 c.c. magnesia mixture. Allow to stand over night. All the arsenic is precipitated as ammonium magnesium arsenate. Antimony remains in solution, being held there by the tartaric acid present. Filter off the ammonium magnesium arsenate, washing with cold water containing a little ammonia, then dry, ignite, and weigh as magnesium pyroarsenate.

454. Acidify the filtrate with hydrochloric acid and precipitate the antimony with hydrogen sulphide as before; filter and wash with hydrogen sulphide water. Separate the antimony sulphide from the filter paper and dissolve the adhering particles with ammonium sulphide, transferring to a beaker. Wash with ammonia and evaporate to dryness on water bath. Carefully add a few drops of nitric acid and then 1 to 2 c.c. of fuming nitric acid to oxidize the antimony. Then evaporate to small bulk for crucible, and heat to dryness on water bath, then ignite at low red heat to constant weight. Weigh as lead sulphate.

455. Method II. Treat ten grams pigment in No. 3-A casserole with about ten grams potassium bisulphate, 10 c.c. nitric acid, 15 c.c. sulphuric acid, and about 0.5 gram tartaric acid. Run to strong fumes; continue heating until all the carbon is destroyed and the solution is clear. Cool, dilute, and boil until soluble sulphates are in solution. Cool, filter, and wash thoroughly. Add tartaric acid and pass hydrogen sulphide gas. Filter off arsenic and antimony sulphides. Dissolve precipitate in potassium hydroxide solution and filter. Pour filtrate into solution of hydrochloric acid (2 to 1). Pass hydrogen sulphide gas and

filter off As_2S_3 on a weighed Gooch crucible. Wash with alcohol and carbon bisulphide to remove sulphur.

456. Neutralize filtrate until Sb_2S_3 begins to precipitate. Dilute with equal volume of water, pass hydrogen sulphide gas, and filter off precipitate, Sb_2S_3 , on a weighed Gooch crucible. Wash with alcohol and carbon bisulphide to remove sulphur. Dry and weigh.

CHAPTER XXVII.

ANALYSIS OF WHITE LEAD AND PAINTS IN OIL.

457. Securing a Fair Sample. There are probably more disagreements and differences between chemists engaged in paint analysis in the resulting analyses obtained than in any other field requiring the services of trained analytical chemists. The writer has seen the results obtained by taking a gallon of a mixed paint of one of the leading brands on the market and dividing it into quarts and sending the four cans to different chemists who made a specialty of paint analysis. The four analyses bore very little observable connection with the formula by which the paint was made or, in fact, with each other. These differences could have arisen from only the following causes:

1. The paint not being compounded strictly according to formula.
2. Chemical changes and loss of some of the volatile constituents in mixing and grinding.
3. Not securing a fair sample for analysis.
4. Inaccurate methods of analysis.

458. Variations from Formula. Where paints are made in large quantities, each mix representing 100 gallons or more, it is a very easy matter for the man who does the weighing or measuring to make a mistake. This is especially true of the liquid constituents, part of which are added before the mix is run through the mill and the remainder in the thinning tank. The keeping in mind the number of gallons of linseed oil, volatile oil, water, etc., added as the workman goes back and forth from the faucets to the mixer

or thinning tanks, is not as easy as it may seem at first glance, especially if the batch is a large one.

459. Chemical Changes in Grinding. The chemical reactions that may occur between different pigments when subjected to the combined action of heat and pressure have not been given the consideration they should by the majority of paint chemists. The day of water-cooled paint mills is here, but there are many paint manufacturers who are yet grinding their various pigments in mills that are not water-cooled, and most of them have but little idea how hot the paste will get toward the close of a day's run; 280° and even 300° F. are not unusual temperatures. The effect of high-temperature grinding on white lead and linseed oil has already been spoken of under the discussion of properties of white lead.

460. The effect of pressure is well illustrated by the following experiment. Using considerable pressure, grind intimately 1 gram of lead sulphate with 3 grams of sodium carbonate for some minutes in an agate mortar, and it will be found that practically all of the lead sulphate has been converted into carbonate and the sodium carbonate into sodium sulphate. Bleached oil carrying traces of sulphuric acid and zinc oxide containing zinc sulphate will certainly react with white lead when ground under pressure at a comparatively high temperature. In this connection the catalytic action of sulphur dioxide, which occurs in greater or less quantities in zinc oxides and especially in leaded zincs, should not be overlooked, especially when these pigments are used in the manufacture of mixed paints.

461. In paint factories where the different operations are under the guidance of a capable chemist, losses arising from evaporation of the volatile thinners in the mixing tanks, etc., should not occur, but there is many a mixed paint that when sealed in the can does not contain the

same percentage of volatile thinners as was originally added.

462. Obtaining an Average Sample. The reason, however, for the majority of the disagreements between paint chemists lies in not securing an average sample for analysis, i.e., the sample taken does not represent the average composition of the paint in the package to be analyzed. This is especially true of mixed paints. The can of paint submitted to the chemist may have been on a store shelf for some months, until the pigments have settled hard in the bottom of the can and the task of breaking them up and recombining them with the oil portion is by no means an easy one. Whenever a sample is received in which the pigments have settled out, the oil portion should be poured off as completely as possible, the remaining paste entirely removed from the can into the mixing can, which should have at least twice the capacity of the sample can. Using a very stiff spatula, break up the paste thoroughly and gradually work the oil portion back into the paste. The first addition of oil should be small and the paste worked thoroughly after each addition. When the oil is all in, the paint should run off from the spatula smoothly without showing any evidence of lumps.

463. Having reduced the paint to uniform consistency, it should be kept tightly covered to prevent loss of the volatile thinners until all the samples necessary for analysis have been taken out, and especial care should be taken to stir the paint thoroughly each time before taking the samples, as the heavier pigments tend to settle more rapidly than those having a lighter specific gravity.

464. Inaccurate Methods of Analysis. Inaccurate methods in making the analysis have doubtless had considerable to do with the disagreements above mentioned. However, much progress has been made in improving

methods during the last few years, so that this consideration does not apply as seriously as formerly.

465. Extraction of the Vehicle. The pigment may be freed from oil in the following type of apparatus, although the Soxhlet extractor may be used if desired. A folded filter paper is inserted in a suitable sized S. & S. thimble, dried in the oven for a few minutes, cooled in the desiccator, and weighed. A weighed amount of the sample reduced to a uniform consistency is introduced into the thimble; 12 to 18 grams will furnish an ample amount of pigment for analysis. Ether can be used to advantage as the volatile solvent when the paint contains little or no water, but for paints containing a considerable amount of water, acetone will be found superior to ether as a solvent. In order to secure as complete a removal of the vehicle as possible, the extraction should continue for 24 hours. In order to reduce the danger from fire, the extractor can be heated with advantage by means of an electrically heated water-bath. After the extraction is complete, the thimble and contents are dried for two to three hours in the steam oven, cooled in the desiccator, and weighed. The loss in weight suffered by the paint represents the amount of vehicle. The pigment is reduced to a uniformly fine powder and placed in a small tightly stoppered sample bottle until required for analysis.

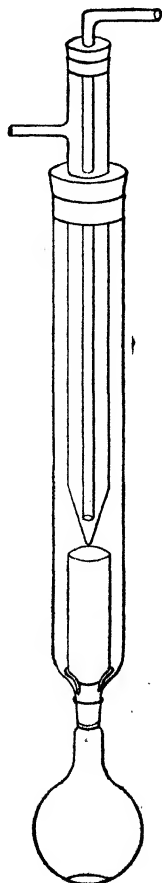


FIG. 84.
EXTRACTION
APPARATUS.

466. Removal of Vehicle for Examination. A conven-

ient method of obtaining sufficient vehicle from a paint for the determination of the volatile oils, the quality of the linseed oil, etc., is to fill a tall cylinder with such of the sample as is not needed for the water estimation (100 to 150 grams) and for obtaining the free pigment, corking it tightly and placing it in a tall copper can filled with water heated to about 70° C. By reducing the viscosity of the oil in this manner the pigment will settle quite rapidly, and in 24 hours, if the temperature is maintained at 70° C., sufficient oil may be siphoned off with the aid of the suction pump. For the removal of volatile oils by distillation with steam at 130° C. and an examination of the linseed oil remaining behind, as well as for the identification and separation of the volatile oils from each other, the reader is referred to the "Analysis of Mixed Paints, Color Pigments, and Varnishes," published by the writer.

467. Use of Centrifuge. By far the most convenient method of obtaining sufficient vehicle for examination is by centrifuging the paint. In the average laboratory an electric centrifuge is the most convenient type. The cylinders used may be of glass, but preferably of aluminum, as the pressure on the ends will often exceed 50 pounds per square inch when the centrifuge is in motion. The bottoms of the cylinders should be removable, being screwed on to the cylinder. This permits of the easy removal of the precipitated paint and the rapid cleaning of the cylinders.

468. It is necessary that the cylinders opposite each other be evenly balanced, and it is always advisable to balance up the cylinders on the scales before placing them in the centrifuge. The cylinders should be tightly corked to prevent loss by evaporation of the volatile thinners, and live steam admitted into the centrifuge chamber sufficient to heat the contents of the tubes to about 70° C.

In the majority of cases the pigment will be thrown out rapidly and cleanly and, by using a number of cylinders, an ample amount of the oils may be easily obtained.

469. In the factory laboratory, where steam pressure is always available, an ordinary steam centrifuge such as is used for the ordinary Babcock butter-fat test is more convenient than the electric machine, as the steam leakage into the upper chambers is sufficient to keep the tubes warm enough to insure the rapid precipitation of the pigment.

470. Use of Volatile Petroleum Thinners. A word may be said in connection with the increased use of volatile petroleum products as paint thinners. In discussing this subject a prominent paint chemist states the problem as follows:

“The rapid depletion of our turpentine forests and the rapid advance in the price of turpentine has brought prominently before every paint and varnish manufacturer the absolute necessity for some volatile solvent capable of replacing entirely or in part the turpentine he used.” The answer to this problem has been, naturally, the flooding of the market with an innumerable number of substitutes of uncertain merit. Some of the smaller paint companies, and especially those making paint for “a price,” have adopted some of these substitutes without a careful investigation of their merits. On the other hand, some of the larger and more completely equipped companies have devoted considerable study to the question of turpentine substitutes, first endeavoring to ascertain the exact function of the turpentine in the paint and then seeking to prepare an article that would have the same essential properties and at the same time be free from objectionable characteristics.

471. According to the views of leading chemists. the

purpose of the turpentine in the paint is to increase the penetration of the oil and pigments into the wood and under coats of paints; to produce a "flat" or "semi-flat" surface, permitting a closer union with the succeeding coat, or for appearance as in the case of paints intended for inside use; to render the paint more fluid without the use of an excessive amount of oil; to increase the speed of the drying of the paint both by evaporation and by oxidation; and finally, to act as a bleaching agent on the oil, rendering the paint whiter; this, however, is not as essential as the other functions of the turpentine. Naturally chemists turned to the various petroleum products in their search for the desired substitute, and as a result of their studies a number of companies are using a product which does not behave like any of the petroleum distillates with which the chemist is ordinarily familiar.

472. Characteristics. This product is used under various trade names and differs slightly in composition according to the petroleum or petroleums from which it is derived, i.e., whether of Texas, Russian, or of some other origin. It is prepared so that it has a flash point slightly above that of turpentine, and hence as a fire risk it is as safe as turpentine, which is in marked contradistinction to benzine. It evaporates cleanly, and at a rate about or slightly slower than ordinary turpentine. In securing penetration of the paint it is fully equal to turpentine and is free from objectionable odors. In order to overcome the deficiency of not assisting the paint in drying by oxidation and the lack of bleaching action on the linseed oil, several paint manufacturers add a sufficient percentage of spirits of turpentine to supply these desired qualities.

473. Reporting Results. The chemist in making an analysis of paints should be very careful in stating the composition of the volatile oils used in the vehicle, and not confound

these turpentine substitutes with ordinary benzine, which costs considerably less than half as much and is dangerous to use on account of the fire risk and is too volatile to be accepted as a proper turpentine substitute. The analysis of these substitutes when once incorporated into the paint is somewhat difficult, but with care may be obtained by distillation as above mentioned. Having secured the volatile distillate and having freed it from all traces of water it may be redistilled, using a small distilling flask and carefully noting the temperatures at which the product passes over. The substitutes of recognized merit distil usually between 150° and 200° C. Any benzine present will pass over below 150° C., and kerosene mostly above 200° C. If the latter is present, however, a large portion will not be volatile in the steam distillation and will remain in the linseed oil, being readily detected in the latter by pouring six drops in a few cubic centimeters of an alcoholic solution of potash, boiling gently for two minutes and pouring into a little distilled water, a decided cloudiness indicating the presence of unsaponifiable petroleum oils.

CHAPTER XXVIII.

ESTIMATION OF WATER IN WHITE LEADS AND PAINTS.

474. Occurrence. A fraction of 1 per cent of water may occur normally in the vehicle. A small percentage, 1 to 3 per cent, may be incorporated into the paint by the manufacturer under the belief that it secures better penetration when applied to surfaces that are slightly damp, and also that it will prevent the pigment from settling hard in the can. Oftentimes, however, large quantities are introduced for the purpose of cheapening the product. The water may be added to the paint and prevented from separating out, by forming an emulsion with the oil with the aid of an alkali, or by grinding it into the pigment, using an adhesive such as glue or casein. In the first case the nature of the ash left on burning some of the separated vehicle will indicate whether an alkali has been used or not. In the second case the vehicle will yield less than one per cent of water when distilled with a dry, inert substance such as sublimed lead, as the water remains with the pigment.

475. Detection. Water may be tested for qualitatively in light-colored paints, by rubbing with a little eosin on a glass plate. If water is present the paint will take on a strong pink color, otherwise the color will remain practically unchanged. If the paint contains considerable coloring material, rendering the eosin test inapplicable, a weighed strip of gelatine may be immersed in the paint for several hours. If water is present the gelatine will soften and increase in weight, the adhering paint being removed by the use of petroleum ether and drying for a

minute or two between sheets of filter paper. An immersion of the gelatine for 18 to 24 hours will show the presence of water in a paint containing as little as 2 per cent.

476. Estimation. Quantitatively, the water may be estimated by distillation, using a retort, the neck of which

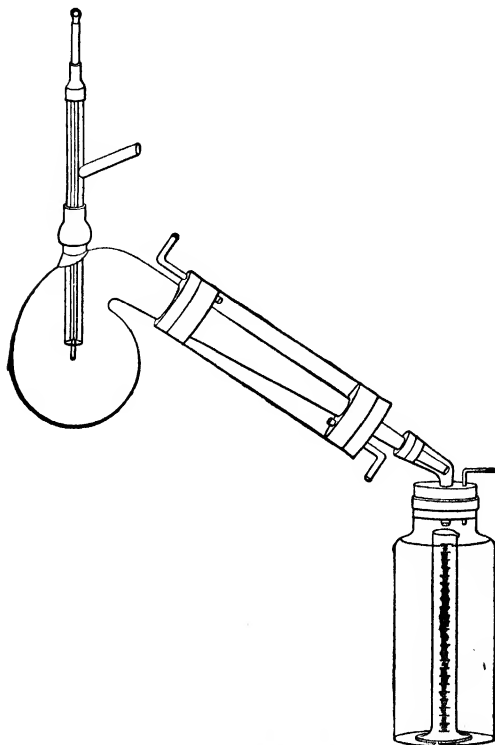


FIG. 85.—ESTIMATION OF WATER.

forms the inner tube of a condenser, the outside tube being a Welsbach chimney. One hundred grams of the paint is weighed into an aluminum beaker and mixed with a thoroughly dried, inert pigment like silica or sublimed

lead until it ceases to be pasty, and then transferred to the retort, which is heated in an oil bath, the water being collected in a graduate calibrated to fifths of cubic centimeters. Toward the end of the distillation, the temperature of the contents of the retort being raised to 200° C., a very slow current of air or illuminating gas is admitted to the retort through a tube passing nearly to the surface of the pigment. This will carry over the last traces of moisture.

477. It is advisable to pass the illuminating gas through a wash-bottle containing sulphuric acid, which not only serves to remove moisture, but acts as an indicator for the rate of flowing gas. The heating should be continued for at least two hours at the above temperature to insure the complete removal of the combined water from the basic carbonate of lead which may be present. This should be deducted from the total amount of water obtained, by multiplying the basic carbonate present by 2.3 per cent, which represents the average per cent of combined water in white lead.

478. It is impossible to remove the water by this method, without decomposing part of the lead hydroxide of the white lead, as it begins to lose the combined water at 105° to 120° C., the total combined water being driven off at 150° C. for 6 hours with little or no loss of carbon dioxide. An exposure of 4 hours at a temperature 175 degrees results in the loss of all the water and a slight amount of carbon dioxide; at 200° degrees an exposure of 2 hours is sufficient to remove all of the combined water and about one-quarter to one-third of the carbon dioxide.

In each case a blank should be run in order to ascertain that the inert pigment and illuminating gas are free from condensable moisture.

The author believes that a current of air obtained by

the use of an aspirator is preferable to the use of illuminating gas, as with the latter there is the possibility of the formation of water from the hydrogen of the illuminating gas and the lead oxide present, if the temperature is raised too high.

479. Estimation of Water with Amyl Reagent. This method, worked out by the author in his laboratory, has given excellent results, not only in mixed paints but also in paste and semi-paste goods. The determination requires only a few minutes and as the combined water of the white lead is not driven off, there is no correction to be applied.

480. Preparation of Amyl Reagent. The components of the amyl reagent — amyl acetate and amyl valerianate — should be as pure as possible, and unless of specified purity an inferior grade is apt to be obtained. Fritsche Bros., New York City, have furnished the most satisfactory article the author has been able to secure. The amyl acetate and valerianate should be washed, before mixing, with at least two changes of pure distilled water at room temperature. This can readily be accomplished in a large separatory funnel. Washing with water will remove practically all of the impurities and such as may remain will be saturated at that temperature. The reagent is prepared by mixing 5 parts of amyl acetate with 1 part of amyl valerianate.

481. Determination. About 100 grams of the thoroughly stirred sample of paint are weighed into a flat-bottomed, 200–250-c.c., side-necked distilling flask. Add 75 c.c. of the amyl reagent and with a gentle rotary motion secure a thorough mixing of the contents of the flask. Connect with an upright condenser and distill over about 60 c.c. of the reagent into a cylinder graduated into tenths of cubic centimeters. When the larger portion of water has passed

over, the upper portion of the flask should be warmed gently with the naked flame, in order to expel the small portion of moisture that will have collected on the sides of the flask. The distillation should then be continued until the requisite amount of reagent has distilled over. The percentage of water can then be easily read off from the graduated cylinder and the contents of the distilling flask will be sufficiently liquid to insure easy removal. With paints high in volatile oils the volume of the distillate should be increased to at least 75 c.c.

482. Practical Example. The following determination with a paint of known water content indicates the satisfactory nature and accuracy of this method.

White lead	115 grams
Linseed oil	40 grams
Turpentine	10 grams
Water	6 grams

were thoroughly mixed, introduced into a side-necked distilling flask, 75 c.c. of the prepared amyl reagent added and the mixture agitated until of uniform consistency. The following distillation figures were obtained:

Temperature.	Water.	Amyl reagent and turpentine.
92°-110° C.	5.5 c.c.	16 c.c.
110°-125° C.	0.9 c.c.	13 c.c.
125°-140° C.	0.0 c.c.	18 c.c.
140°-145° C.	0.0 c.c.	14 c.c.
	6.4 c.c.	61 c.c.

The same mixture without the addition of water gave 0.3 c.c. of water when run as a blank.

Theoretical percentage of added water 3.51

Percentage of water obtained (corrected) . . . 3.56

CHAPTER XXIX.

QUALITATIVE ANALYSIS OF COMBINATION WHITE LEADS AND PASTES.

483. Classification. The various pigments to be found in "combination leads," base whites and the various mixed paints may be divided into two classes, the so-called active pigments and the inert pigments.

The active pigments comprise

White lead.

Sublimed white lead.

Zinc oxide.

Zinc lead white.

Leaded zines and

Lithopone.

The inert pigments comprise

Barium sulphate (Barytes, Blanc fixé).

Barium carbonate.

Calcium carbonate. (Whiting, Paris white, White mineral primer).

Calcium sulphate (Gypsum, Terra alba).

China clay (Kaolin).

Asbestine (Magnesium silicate).

Silica (Silex).

The properties of the various active pigments have been discussed under their methods of manufacture and need not be taken up here.

484. Inert Pigments. The inert pigments have widely different properties not only from a chemical standpoint but from a physical standpoint as well, and while two pigments may have the same chemical composition they

may differ greatly in physical properties, producing entirely different results when used in paints. Hence it is practically impossible to judge service values of paints containing inert pigments from the chemical analysis. Chemical analysis, however, in conjunction with a careful microscopic examination, especially if a polarizing microscope be used, may give some idea of what the service value should be.

485. Barium Sulphate (Barytes, Blanc Fixé). Barytes is perhaps the most extensively used of the inert pigments. It more nearly approximates white lead in specific gravity and oil-taking capacity than any of the others. It is absolutely unaffected by acids, alkalis or atmospheric influences of any kind. Its hiding power or opacity when ground in oil is very low, and hence when used in any considerable percentage in a mixed paint or combination lead its presence is indicated by the reduced opacity of the paint film. The requisites of a high grade of barytes are whiteness and fineness. The cheaper grades of barytes have a yellowish gray color and are often treated with sulphuric acid to improve the color by removing the iron. A considerable portion of the barytes on the market is "blued," either by precipitating the iron sulphate obtained by the treatment with the sulphuric acid as Prussian blue, or adding the Prussian or ultramarine blue separately. The majority of paint manufacturers, however, prefer to blue their goods themselves, if necessary, during the process of manufacture. The fineness with which barytes has been ground can be easily determined by examination under the microscope after the acid soluble pigments have been dissolved out.

486. Blanc fixé is a precipitated barium sulphate. Owing to its more amorphous character it has a much greater hiding power than barytes. Its oil-taking capacity

is greater; it does not settle in a paint as badly as barytes and is much whiter; its cost, however, is about twice as great. It is largely used as an inert base for organic lakes.

487. Barium Carbonate. This pigment is used comparatively little in the United States as a paint pigment. In physical and chemical properties it much resembles white mineral primer, a form of calcium carbonate, although it does not require as much oil in grinding. Its specific gravity is about that of barytes. It dissolves readily in acetic, nitric and hydrochloric acids; sulphuric acid converts it slowly into insoluble barium sulphate. In the hundreds of mixed paints examined by the writer barium carbonate was found to be present in only one paint, although its presence in certain organic lakes is not uncommon in a precipitated form.

488. Calcium Carbonate, Paris White, Whiting, Alba Whiting, White Mineral Primer.

Under the heading of calcium carbonate we have three distinct classes of pigments. Those obtained from

1. English cliffstone or similar chalk formations such as Paris white, gilders' whiting and commercial whiting.

2. Marble or a crystalline calcium carbonate such as marble dust, white mineral primer, etc.

3. Precipitated calcium carbonate such as alba whiting.

489. The English cliffstone pigments are usually put on the market in about three grades. The first grade is the whitest and most finely ground and bolted and is usually sold under some such name as Paris white, and finds its use largely in first quality mixed paints and combination leads. The second grade is slightly coarser and has a slightly grayish tint and is usually sold under some such name as gilders' whiting. It is also usually bolted, and is used in second and third grade paints. The third grade

is inferior in color and fineness to the other two grades. It finds its chief use in kalsomine; although it is used in some of the very inferior paints, it never should be, owing to the fact that it is not bolted, and therefore contains some relatively large particles. It is usually sold as commercial whiting.

490. The various forms of white mineral primer are of an entirely different nature physically from the cliffstone products, being fragments of small crystals. They have very little body in oil, being nearly transparent. They are usually whiter than Paris white and possess much greater tooth, but are not much used in mixed paints owing to the fact that they settle badly in the can and have very little opacity. They find their chief use in primers and in putty for making it work shorter. Being of a crystalline nature it is natural that they require less oil in grinding than Paris white.

Alba whiting and other precipitated calcium carbonate pigments are very white, but being very light and fluffy require an enormous amount of oil in grinding.

While it is not an easy matter to distinguish these different products in a paint, yet the microscope is of much value in determining the fineness of grinding.

491. Calcium Sulphate (Gypsum, Terra Alba). This pigment is found in combination white leads and exterior white paints only to a limited extent. Its chief use seems to be in certain lines of railroad paints and in dipping or implement paints. It is also used to some extent as a base for striking certain organic lakes upon, notably the para reds. The writer, despite the favorable opinions of many eminent paint authorities, does not believe that calcium sulphate, or gypsum, as it is more commonly known, is adapted for use in exterior paints owing to its solubility in water, it being soluble about one part in five

hundred. A linseed oil paint film is by no means impervious to moisture and the continued action of rains and storms cannot be otherwise than unfavorable, as the solvent action of the water in removing a portion of the gypsum renders the paint film more porous and its disintegration more rapid.

492. Venetian reds often contain fifty to eighty per cent of calcium sulphate. The better class of Venetian reds are composed of fifty per cent of ferric oxide and fifty per cent of calcium sulphate. This calcium sulphate should not be confounded with the forms above discussed, as it has been subjected to the action of a high heat and is, therefore, insoluble in water, and is regarded as a proper constituent of Venetian reds.

493. Aluminum Silicate (China clay, Kaolin, Tolanite). This pigment also finds but little use in combination white leads owing to its low specific gravity. It is, however, used extensively in mixed paints, implement paints, and as an inert base for striking para and other organic reds upon, especially for colors which are used in dipping paints. Its functions and properties are very similar to those of magnesium silicate, it being essentially a suspender for preventing settling in paints. It is very inert in its action with acids and alkalies. Strong hydrochloric acid with continued boiling will dissolve a very slight fraction of one per cent, hence traces of aluminum may be found in a hydrochloric acid solution of a paint containing aluminum silicate. Some of the silicates much in favor with the paint trade contain a considerable percentage of what is apparently uncombined silica. In mixed paints it is often used with magnesium silicate. Hence a microscopic examination is usually required to determine whether the latter is present or not. It yields to treatment by fusion with sodium carbonate more readily than magnesium silicate.

When subjected to a high temperature it loses eleven to thirteen per cent of water of hydration.

494. Magnesium Silicate (Asbestine pulp, Talcose). This pigment is sold under the various names of white silicate, asbestine, asbestine pulp, etc. Large amounts are obtained from natural deposits in and around Gouverneur, N. Y. It has a very low specific gravity, and is much used in lead and zinc paints to prevent those pigments from settling hard in the bottom of the package. Chemically it is very inert, being unacted upon by any of the ordinary acids. It is, however, decomposable with hydrofluoric acid in a platinum dish and by fusion with sodium carbonate. Fusion with potassium bisulphate decomposes it only partially. Continued heating at a bright red heat will cause a loss of three to five per cent in weight, due to loss of water of hydration. It is easily recognized under the microscope by the fibrous or rod-like structure of the particles.

495. Silica (Silex). There are two distinct kinds of silica to be found on the market, that obtained from crushed quartz, which is a very pure form of silica, and an impure form found in natural deposits especially in Illinois. The former possesses a very pronounced "tooth;" under the microscope the particles are very sharp and jagged, and it is quite transparent in oil. The second form is composed of rounded particles of a complex chemical nature; besides free silica there are usually found associated with it calcium carbonate, aluminum silicate and magnesium silicate, besides a small amount of magnesium carbonate. This product requires more oil in grinding, and has much more body, but considerably less tooth.

496. In the majority of cases a complete qualitative analysis of the pigments present is hardly worth the time it requires, as there is but little time lost in following the regular quantitative scheme. If, however, a qualitative analy-

sis is desired, the following outline will be found sufficient in most instances, the removal of the vehicle previous to these tests being understood.

497. Carbonates. Effervescence with concentrated hydrochloric acid indicates carbonates, or hydrogen sulphide if zinc sulphide be present, the latter being distinguished by its odor and by the fumes blackening a piece of filter paper moistened with lead acetate.

498. Barytes, Silica, Clay, or other Silicates. Boil above mixtures five minutes, dilute with boiling water, filter. An insoluble residue may be barytes, silica, clay, or other silicates. Test for barytes with flame test, using a platinum wire. A characteristic green color indicates barium.

499. Sulphates. Test a small portion of the acid filtrate for combined sulphuric acid with a few drops of barium chloride.

500. Lead. Test another small portion of the acid filtrate with sulphuric acid. A white precipitate at once or on standing indicates lead.

501. Zinc. Take another small portion of the acid filtrate and add a few drops of potassium ferrocyanide. A white precipitate with a bluish tinge indicates zinc.

502. Calcium. The remaining portion of the acid filtrate is made alkaline with ammonia and hydrogen sulphide passed in for five minutes. Filter and test filtrate for calcium with ammonium oxalate, setting aside in a warm place.

503. Magnesium. After completely precipitating the calcium, add a few drops of hydrogen sodium phosphate. A precipitate on standing indicates the presence of magnesium compounds.

The identification of the forms in which the lead may occur can only be determined by the quantitative scheme if both sulphates and carbonates are present.

CHAPTER XXX.

QUANTITATIVE ANALYSIS OF COMBINATION WHITE LEADS AND PAINTS.

504. Total Lead. Weigh 1 gram of the dry pigment into a 250-c.c. beaker. Add 30 c.c. of strong hydrochloric acid, boil 5 minutes, add 50 c.c. of hot water, heat 15 minutes longer, settle, filter while hot, and wash thoroughly with boiling water. The washing should be begun the instant the solution has filtered through, in order to avoid any crystallization of lead chloride in the pores of the filter paper. Once formed the crystals can only be dissolved with difficulty and with the use of an excess of wash water, which, as stated, must be at boiling temperature. This operation is best conducted by the aid of suction. Casein and other products of a similar nature are occasionally used in the manufacture of mixed paints in considerable quantities, and the analyst should always be on the lookout for the possible presence of these substances.

505. The solution is made just alkaline with ammonia, then just acid to litmus with hydrochloric acid. It is very necessary that the solution be only barely acid, as a comparatively small quantity of free acid will keep considerable lead from precipitating. Having been made barely alkaline, which is indicated by the precipitation of the lead, the solution is brought to a faintly acid condition by using dilute hydrochloric acid (1 to 10). Dilute to about 350 c.c. Cool, pass in hydrogen sulphide gas, noting the color of the precipitate; if gray, some zinc is being thrown down; if reddish black, the solution is too acid; add a few drops of dilute acid or ammonia as the case requires. Settle, filter, and wash with cold water.

506. Place filter and precipitate in 25 c.c. of nitric acid and 25 c.c. of water, heat gently until the lead has all dissolved as shown by the residual sulphur having a yellow to whitish color. Do not boil hard enough to thoroughly disintegrate the filter paper. If difficulty is experienced in dissolving the lead contained in the sulphur particles, it is better to collect them into a ball with the aid of a stirring rod and remove to a small beaker and treat with a few cubic centimeters of concentrated nitric acid, and heat until dissolved, then pour back into the larger beaker.

507. Pour solution and filter paper on to a suction funnel provided with a platinum cone. If any fine particles pass through, pour the filtrate back again. This procedure permits the washing of the filter mass with a very small amount of water, thus saving considerable time in the subsequent evaporation. Add 5 c.c. of dilute sulphuric acid to filtrate, and evaporate until sulphur trioxide fumes appear. Cool, add 25 c.c. of water, 25 c.c. of alcohol; allow to stand one-half hour with occasional stirring; filter, using Gooch crucible, wash with dilute alcohol, dry, heat gently over ordinary lamp, and weigh as lead sulphate.

508. Calcium. The filtrate containing the zinc, calcium, and possibly magnesium is made slightly alkaline with ammonia, a few drops of a mercuric chloride solution (1 to 10) added, and a stream of hydrogen sulphide gas passed into the solution for about ten minutes.

The addition of the mercuric chloride renders the precipitate granular and very easy to filter, and entirely obviates the difficulty of filtering a slimy zinc sulphide precipitate. In the analysis of tints where the zinc cannot be titrated until it has been freed from iron, the addition of the mercuric chloride will not cause any trouble,

as treatment with hydrochloric acid results in the solution of the zinc only, the mercuric sulphide being insoluble in hydrochloric acid. Settle, decant, filter, and wash.

509. Evaporate the filtrate from above precipitate to about 150 c.c., make alkaline with ammonia, add ammonium oxalate (50 c.c. for 1 gram of lime), usually 20 c.c. is sufficient, and set in a warm place for two or three hours. Filter, wash, ignite, and weigh as calcium oxide, or titrate precipitate with permanganate by placing filter and precipitate in a 400-c.c. beaker, adding 200 c.c. of boiling water and 25 c.c. of dilute sulphuric acid, and titrate with standard tenth-normal potassium permanganate.

1 c.c. tenth-normal permanganate = 0.0028 gram CaO.

1 c.c. tenth-normal permanganate = 0.0050 gram CaCO₃.

Barium carbonate is still to be found in certain mixed paints, and it is advisable to test for the presence of soluble barium before precipitating the calcium.

510. Magnesium. The filtrate from the calcium oxalate should be tested for magnesium, by treating with hydrogen sodium phosphate. Allow to stand one-half hour, add 25 c.c. of ammonia, allow to stand one hour, then filter on to a Gooch crucible, wash with dilute ammonia, ignite, and weigh.

Weight precipitate \times 0.7575 = weight magnesium carbonate.

511. Zinc Oxide. Reagents. Standard Zinc Solution. Dissolve 10 grams of chemically pure zinc in hydrochloric acid in a graduated liter flask, add 50 grams of ammonium chloride and make up to one liter.

1 c.c. = 0.01 gram zinc or 0.01245 gram zinc oxide.

512. Standard Potassium Ferrocyanide Solution. Dissolve 46 to 48 grams of crystallized potassium ferrocyanide in water, make to 1000 c.c.

513. Uranium Nitrate Solution. Dissolve 15 grams of uranium nitrate in 100 c.c. of water.

514. Standardizing the Ferrocyanide Solution. To determine the value of the potassium ferrocyanide solution, pipette 25 c.c. of the zinc solution into a 400 c.c. beaker. Dilute somewhat and make faintly alkaline with ammonia, bring to a faintly acid condition with hydrochloric acid, and then add 3 c.c. excess of the concentrated acid, dilute to a total volume of about 250 c.c., heat to 80° C. and titrate as follows: Pour off about 10 c.c. of the zinc solution into a small beaker and set aside, run the ferrocyanide into the remainder from a burette, a few cubic centimeters at a time, until the solution takes on a slight ash gray color, or until a drop of the solution placed in contact with a drop of the uranium nitrate solution on a porcelain plate turns to a distinct brownish color. Often the end point has been passed by quite a little.

515. The 10 c.c. of zinc solution that has been reserved is now added and the titration continued, drop by drop, testing a drop of the solution carefully on the porcelain plate after each addition of ferrocyanide solution. Some little time is required for the test drop to change color, so that the end point may have been passed slightly. This may be corrected for by making a memorandum of the burette readings, having the test drops arranged in regular order and taking as the proper reading the one first showing a distinct brownish tinge. Having noted the number of cubic centimeters of ferrocyanide required for the titration of the standard zinc solution, the value of 1 c.c. may be readily calculated.

516. Titration of Sample. One-half gram of the sample, if high in zinc, or 1 gram, if the zinc content is fairly low, is dissolved in a covered beaker in 10 c.c. of hydrochloric acid and 10 c.c. of water, the solution diluted and treated

exactly as described above for the standard zinc solution, care being taken to titrate to exactly the same depth of color on the porcelain test plate. If the method is carefully carried out, the procedure being uniformly the same in each determination, the results will be found satisfactorily accurate.

517. Lead Sulphate. Dissolve 0.5 gram in water, 25 c.c. hydrochloric acid in light excess. Dilute to 200 c.c. and add a piece of aluminum foil which about covers the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, ignite, and weigh as barium sulphate. Calculate to lead sulphate by multiplying by 1.3 as a factor, unless calcium sulphate is present, in which case it is advisable to make use of Thompson's separation.

518. In the absence of barium sulphate, the combined sulphuric acid may be estimated by H. Mannhardt's method: Grind 1 gram of pigment with 1 gram of sodium carbonate, very intimately in an agate mortar. Boil gently for ten minutes, the combined sulphuric acid, and in the case of colors containing chromates, the chromic acid will pass into solution and may be estimated in the filtrate in the usual manner. If necessary collect the insoluble portion on a filter, dry, detach and triturate a second time.

519. Basic Carbonate of Lead (White lead). After deducting the amount of lead present in the pigment as sulphate of lead, calculate the rest of the lead as white lead by multiplying the remaining sulphate by 0.852, unless sublimed lead is suspected to be present, in which case the combined lead oxide must be taken into consideration.

520. Insoluble Residue. The insoluble residue from the original hydrochloric acid treatment may contain barytes, magnesium silicate, silica and clay. Ignite, filter paper and residue until white, weigh as total insoluble matter; grind in agate mortar with about 10 times its weight of sodium carbonate, fuse for 1 hour in a platinum crucible, and dissolve out in hot water.

521. Barium Sulphate. The solution from the fusion is filtered. The residue consists of barium carbonate, magnesium carbonate, etc., and is washed with hot water. The filtrate and washings are saved. Pierce filter paper and wash precipitate into clean beaker with hot dilute hydrochloric acid; finish washing with hot water, heat to boiling, add 10 c.c. of dilute sulphuric acid to precipitate barium, filter, ignite, and weigh as barium sulphate.

522. Silica. The filtrate from the barium sulphate is added with care to the filtrate reserved in the preceding paragraph, making distinctly acid; evaporate to complete dryness, cool, add 15 c.c. of hydrochloric acid, heat to boiling, cool, settle, filter, ignite, and weigh as silica.

523. Alumina. The filtrate from the silica will contain all of the alumina except that which was dissolved in the original treatment with hydrochloric acid. This is quite constant, varying from .004 to .005 gram per gram of clay. The acid filtrates are made slightly alkaline with ammonia, and boil until odor disappears. Settle, filter, wash, ignite, and weigh as alumina.

Weight alumina \times 2.5372 = weight clay.

Weight clay \times .4667 = weight of silica in clay.

Any difference greater than 5 per cent may be considered as free or added silica, according to Scott.

524. Calcium and Magnesium Oxides. If qualitative test shows presence of magnesium in insoluble residue

from the first hydrochloric acid treatment it was present probably as magnesium silicate. Treat filtrate from the aluminum hydroxide for calcium and magnesium oxides. Magnesium silicate contains 3-5 per cent combined water.

525. Hydrofluoric Acid Treatment. Instead of resorting to fusion with sodium carbonate, the insoluble residue, which should be weighed up in a clean platinum crucible, may be treated with several drops of pure concentrated hydrofluoric acid and of sulphuric acid and heated gently on a sand bath under the hood, using only sufficient heat to slowly volatilize the silica and sulphuric acid. Dissolve out in water acidulated with hydrochloric acid. The residue, which is barium sulphate, is filtered off and estimated as such. The filtrate will contain any aluminum, calcium and magnesium present and which may be estimated and calculated as oxides as above described. The combined weight of the barium sulphate, alumina, calcium and magnesium oxides subtracted from the weight of the insoluble residue used gives the weight of silica. This operation is much shorter than resorting to a fusion.

526. Mixed Carbonates and Sulphates. Occasionally paints are met with which contain calcium sulphate, calcium carbonate, sulphate of lead and white lead (basic carbonate of lead), in which case it is necessary to make a separation of the calcium compounds, which may be effected by Thompson's method as follows:

527. To 1 gram of the sample are added 20 c.c. of a mixture of nine parts alcohol (95 per cent) and one part of concentrated nitric acid. Stir, and allow to stand 20 minutes. Decant on a filter and repeat the treatment with the acid-alcohol mixture four times, allowing it to stand each time before decanting. The calcium carbonate will go into solution, while the calcium sulphate or gypsum remains undissolved. Add filter and contents to the

residue remaining in the beaker ; dissolve in hydrochloric acid with sufficient water to insure the solution of the calcium. Make alkaline with ammonia, pass in hydrogen sulphide for 10 minutes, boil, settle, filter. The filtrate and washings are concentrated to about 150 c.c. and the calcium precipitated with ammonium oxalate in the usual manner. The ignited precipitate is calculated to hydrated calcium sulphate.

528. Calculations. The ignited precipitate of calcium oxide obtained from the portion insoluble in the acid-alcohol mixture is subtracted from the total calcium weighed as oxide; the remaining calcium oxide is calculated to calcium carbonate. The total carbon dioxide is determined in a portion of the sample, the portion due to the calcium carbonate is deducted from the total amount, and the remainder calculated to basic carbonate of lead. The combined sulphuric acid due to the sulphate of lime is deducted from the total combined sulphuric acid, and the remainder calculated to sulphate of lead.

Wt. calcium oxide \times 3.0715 = hydrated calcium sulphate.

Wt. calcium oxide \times 1.784 = calcium carbonate.

Wt. calcium carbonate \times 0.440 = carbon dioxide.

Wt. carbon dioxide \times 8.8068 = basic carbonate of lead.

Wt. of hydrated sulphate of lime \times 0.4561 = combined sulphuric acid.

Wt. of combined sulphuric acid \times 3.788 = sulphate of lead.

CHAPTER XXXI.

LABORATORY EQUIPMENT AND MANIPULATION.

529. The two essential requisites required of a paint chemist are *accuracy* and *rapidity*. Often a pigment or combination of pigments in oil or other thinners is brought into the laboratory and a complete analysis desired on the same day. Unless the laboratory is equipped with all possible labor and time-saving devices this will prove generally impossible. To the experienced paint chemist many of these devices naturally suggest themselves, but to the young chemist who is just beginning his paint work the following points, which have been of assistance to the author in his laboratory work, may be of interest.

530. Weight per Gallon. The use of the "cubic inch" with counterpoise weight will serve for this determination excellently.

531. Specific Gravities. Special hydrometers reading 0.850 to 0.900 and 0.900 to 0.950 can be secured which will afford the desired accuracy with ordinary paint vehicles. For other determinations the Westphal balance should be used.

532. Rapid Extraction of Pigment. The pigment can be rapidly freed from the vehicle by the use of a steam-heated high-speed centrifuge. The cylinders should be of aluminum provided with screw bottoms, rendering the removal of the pigment easy. The use of several of these cylinders, tightly corked, will afford sufficient vehicle for estimation of the amount and nature of volatile oils present. The centrifuge should be strongly constructed, as the pressure on the containing cups due to centrifugal force may

reach 100 pounds to the square inch. If only the pigment is desired, thinning the sample with benzine before centrifuging will materially hasten the operation. On removal from the tubes the pigment should be washed slightly with benzine or acetone on a suction filter.

533. Estimation of Water in Paints. This estimation may be accurately performed in a very few minutes by use of the amyl reagent as described in Chapter XXVIII.

534. Estimation of Volatile Oils. This determination can be made very rapidly by distilling with steam at 130° C. as described in "Analysis of Mixed Paints, Color Pigments and Varnishes," Holley and Ladd, page 39. The apparatus for this determination should have an allotted place in the laboratory and be kept set up ready for use.

535. Rapid Drying. A double wall copper drying oven, to which is attached a Soxhlet ball condenser, a soldered connection being preferable, possesses obvious advantages over the more ordinary type of water oven, especially if a suitable mixture of toluene and xylene, boiling at 115° C., be used instead of water. This will assure a very rapid drying of any material in the oven and the top of the oven will serve as an excellent substitute for a hot plate for evaporations. The oven should be set in a small lead pan so as to avoid danger of fire in case of a leakage.

536. Filtering by Suction. Much time is saved by using the filter pump whenever possible. It also reduces the amount of wash water required so that the resulting filtrates will not be too bulky for convenient handling or require concentration before undergoing further treatment. Instead of the ordinary filter-bottle or flask, a 500 to 1000-c.c. separatory funnel of the conical type can be used to advantage, it being supported by a clamp attached to the neck. The advantage consists in the fact that the filtrate can easily be drawn off from the bottom

without disturbing the funnel containing the precipitate, which is advantageous in the treatment of precipitates which tend to pass through the filter-paper, especially when subjected to washing, as for example chromium hydroxide, or when it is desired to examine a portion of the filtrate before completing the filtration.

537. Use of Gooch Crucible. The Gooch crucible affords the most rapid method for obtaining precipitates in the most desirable form for drying or ignition. Many precipitates which pass through an ordinary Gooch crucible, as for example barium sulphate, can be easily retained by inserting a disk of ashless filter paper on the layer of asbestos after the weighing of the crucible if it is to be subsequently ignited. This disk should be cut slightly larger than the crucible so that when moistened and fitted down tightly, it will be rimmed up slightly all around the edge. In collecting gelatinous precipitates the Gooch should not be allowed to suck dry until the filtering operation is completed.

538. The preparation of the asbestos for use in the Gooch crucible is a most important item. The short-fiber asbestos sold for this purpose by the chemical supply houses should be shaken up in a large bottle of water, the heavy fibers allowed to settle for two or three seconds, the contents then poured into another bottle, leaving the heavy fibers behind, then allowed to settle until all but the finest particles have been deposited, which are then poured off, leaving a medium-fiber asbestos which when treated by boiling with hydrochloric acid to remove iron and any other impurities soluble in acid is excellently adapted for rapid filtering.

539. Bottles for Standard Solutions. Many of the standard solutions used in paint analysis, such as potassium ferrocyanide, permanganate, sodium thiosulphate, etc.,

have to be frequently restandardized on account of the effect of light upon them unless kept in a dark closet, which is not always easy to manage. By giving the bottles two coats of an opaque, quick-drying black paint, the solutions will keep their strength for considerable intervals of time, even in a strong light.

APPENDIX.

540. Table I. Atomic Weights.¹

Name.	Symbol.	O = 16.	H = 1.
Aluminium	Al	27.1	26.9
Antimony	Sb	120.2	119.3
Argon	A	39.9	39.6
Arsenic	As	75.0	74.4
Barium	Ba	137.4	136.4
Bismuth	Bi	208.5	206.9
Boron	B	11.0	10.9
Bromine	Br	79.96	79.36
Cadmium	Cd	112.4	111.6
Cæsium	Cs	132.9	131.9
Calcium	Ca	40.1	39.8
Carbon	C	12.0	11.91
Cerium	Ce	140.25	139.2
Chlorine	Cl	35.45	35.18
Chromium	Cr	52.1	51.7
Cobalt	Co	59.0	58.56
Columbium	Cb	94.0	93.3
Copper	Cu	63.6	63.1
Erbium	E	166	164.8
Fluorine	F	19.0	18.9
Gadolinium	Gd	156.0	155.0
Gallium	Ga	70.0	69.5
Germanium	Ge	72.5	71.9
Glucinum	Gl	9.1	9.03
Gold	Au	197.2	195.7
Helium	He	4.0	4.0
Hydrogen	H	1.008	1.0
Indium	In	114.0	113.1
Iodine	I	126.85	125.9
Iridium	Ir	193.0	191.5
Iron	Fe	55.9	55.5
Krypton	Kr	81.8	81.2
Lanthanum	La	138.9	137.9
Lead	Pb	206.9	205.35
Lithium	Li	7.03	6.98
Magnesium	Mg	24.36	24.18
Manganese	Mn	55.0	54.6
Mercury	Hg	200.0	198.5
Molybdenum	Mo	96.0	95.3

¹ J. Am. Chem. Soc., xxvi, 3.

Table I (Continued).

Name.	Symbol.	O = 16.	H = 1.
Neodymium.....	Nd	143.6	142.5
Neon.....	Ne	20.0	19.9
Nickel.....	Ni	58.7	58.3
Nitrogen.....	N	14.04	13.93
Osmium.....	Os	191.0	189.6
Oxygen.....	O	16.0	15.88
Palladium.....	Pd	106.5	105.7
Phosphorus.....	P	31.0	30.77
Platinum.....	Pt	194.8	193.3
Potassium.....	K	39.15	38.86
Praseodymium.....	Pr	140.5	139.4
Radium.....	Ra	225.0	223.3
Rhodium.....	Rh	103.0	102.2
Rubidium.....	Rb	85.4	84.8
Ruthenium.....	Ru	101.7	100.9
Samarium.....	Sm	150.0	148.9
Scandium.....	Sc	44.1	43.8
Selenium.....	Se	79.2	78.6
Silicon.....	Si	28.4	28.2
Silver.....	Ag	107.93	107.12
Sodium.....	Na	23.05	22.88
Strontium.....	Sr	87.6	86.94
Sulphur.....	S	32.06	31.83
Tantalum.....	Ta	183.0	181.6
Tellurium.....	Te	127.6	126.6
Terbium.....	Tb	160	158.8
Thallium.....	Tl	204.1	202.6
Thorium.....	Th	232.5	230.8
Thulium.....	Tm	171	169.7
Tin.....	Sn	119.0	118.1
Titanium.....	Ti	48.1	47.7
Tungsten.....	W	184	182.6
Uranium.....	U	238.5	236.7
Vanadium.....	V	51.2	50.8
Xenon.....	X	128.0	127.0
Ytterbium.....	Yb	173.0	171.7
Yttrium.....	Yt	89.0	88.3
Zinc.....	Zn	65.4	64.9
Zirconium.....	Zr	90.6	89.9

541. Table II. Formulas and Molecular Weights.

Name.	Formula.	Mol. Wt.
Acid, acetic.....	$\text{HC}_2\text{H}_3\text{O}_2$	60
Acid, arsenious.....	H_3AsO_3	125.9
Acid, boric.....	H_3BO_3	62
Acid, citric.....	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$	210
Acid, hydrochloric.....	HCl	36.4
Acid, hydrosulphuric.....	H_2S	34
Acid, nitric.....	HNO_3	63
Acid, nitrous.....	HNO_2	47
Acid, oleic.....	$\text{HC}_{17}\text{H}_{33}\text{O}_2$	282
Acid, oxalic.....	$\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$	126
Acid, sulphuric.....	H_2SO_4	98
Acid, sulphurous.....	H_2SO_3	82
Acid, tannic.....	$\text{C}_{14}\text{H}_{10}\text{O}_9$	322
Acid, tartaric.....	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	150
Amyl acetate.....	$\text{C}_5\text{H}_{11}\text{C}_2\text{H}_3\text{O}_2$	130
Antimony chloride.....	SbCl_3	226.2
Antimony oxide.....	Sb_2O_3	288
Antimony sulphide.....	Sb_2S_3	336
Arsenious oxide.....	As_2O_3	309.8
Arsenious sulphide.....	As_2S_3	245.8
Barium carbonate.....	BaCO_3	196.8
Barium chloride.....	$\text{BaCl}_2 + 2\text{H}_2\text{O}$	243.6
Barium nitrate.....	$\text{Ba}(\text{NO}_3)_2$	260.8
Barium sulphate.....	BaSO_4	232.8
Benzole.....	C_6H_6	78
Calcium carbonate.....	CaCO_3	100
Calcium hydroxide.....	$\text{Ca}(\text{OH})_2$	74
Calcium sulphate.....	CaSO_4	136
Calcium sulphate, crystallized.	$\text{CaSO}_4 + 2\text{H}_2\text{O}$	172
Carbon dioxide.....	CO_2	44
Carbon disulphide.....	CS_2	76

Table II (Continued).

Name.	Formula.	Mol. Wt.
Chromium trioxide.....	CrO_3	100.4
Copper sulphate.....	$\text{CuSO}_4 + 5\text{H}_2\text{O}$	249.2
Cuprous oxide.....	Cu_2O	142.4
Glycerin.....	$\text{C}_3\text{H}_5(\text{OH})_3$	92
Lead acetate.....	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$	378.5
Lead acetate, basic.....	$\text{Pb}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_2$	547
Lead carbonate, basic.....	$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	773.5
Lead carbonate, normal.....	PbCO_3	266.5
Lead chromate.....	PbCrO_4	323.0
Lead dioxide.....	PbO_2	238.5
Lead nitrate.....	$\text{Pb}(\text{NO}_3)_2$	330.5
Lead oxide.....	PbO	222.5
Lead, red oxide of.....	Pb_3O_4	683.5
Lead sulphate.....	PbSO_4	302.5
Potassium bichromate.....	$\text{K}_2\text{Cr}_2\text{O}_7$	294.8
Potassium carbonate.....	$\text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$	330.0
Potassium chromate.....	K_2CrO_4	194.4
Potassium ferrocyanide.....	$\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{H}_2\text{O}$	421.9
Potassium hydroxide.....	KOH	56
Potassium iodide.....	KI	165.6
Potassium permanganate.....	KMnO_4	157
Silver nitrate.....	AgNO_3	169.7
Sodium acetate.....	$\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$	136
Sodium arseniate.....	$\text{Na}_2\text{HASO}_4 + 7\text{H}_2\text{O}$	312
Sodium borate.....	$\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$	382
Sodium carbonate, dry.....	Na_2CO_3	106
Sodium carbonate, crystallized.....	$\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$	286
Sodium nitrate.....	NaNO_3	85
Zinc oxide.....	ZnO	80.9
Zinc sulphate.....	$\text{ZnSO}_4 + 7\text{H}_2\text{O}$	286.9
Zinc sulphide.....	ZnS	96.9

542. Table III. Factors for Gravimetric Analysis.

Determined as	Required.	Factor.
Al ₂ O ₃	Al	0.5303
As ₂ S ₃	As	0.6093
As ₂ S ₃	As ₂ O ₃	0.8043
Mg ₂ As ₂ O ₇	As ₂ O ₃	0.6372
BaSO ₄	Ba	0.5885
BaSO ₄	PbSO ₄	1.3004
BaSO ₄	CaSO ₄	0.5837
BaSO ₄	CaSO ₄ ·2H ₂ O	0.7382
BaSO ₄	SO ₃	0.3433
BaSO ₄	SO ₂	0.2747
CaO.....	Ca	0.7143
CaO.....	CaCO ₃	1.784
CaCO ₃	CO ₂	0.440
CaO.....	CaSO ₄ ·2H ₂ O	3.0715
CaSO ₄ ·2H ₂ O.....	SO ₃	0.4561
CO ₂	2PbCO ₃ ·Pb(OH) ₂	8.8068
Cr ₂ O ₃	PbCrO ₄	4.2288
Cr ₂ O ₃	CrO ₃	1.3137
Cr ₂ O ₃	PbCrO ₄ ·PbO	7.1438
Fe ₂ O ₃	Fe	0.7000
K ₂ SO ₄	K	0.4491
K ₂ PtCl ₆	K	0.1612
K ₂ PtCl ₆	K ₂ O	0.1941
Mg ₂ P ₂ O ₇	Mg	0.2188
Mg ₂ P ₂ O ₇	MgO	0.3624
Mg ₂ P ₂ O ₇	MgCO ₃	0.7575
Na ₂ SO ₄	Na	0.3243
Na ₂ SO ₄	Na ₂ O	0.4368
PbSO ₄	Pb	0.6832
PbSO ₄	PbO	0.7359
PbSO ₄	Pb ₂ O ₄	0.7536
PbSO ₄	2PbCO ₃ ·Pb(OH) ₂	0.8526
PbSO ₄	PbCrO ₄	1.0676
Mg ₂ P ₂ O ₇	P ₂ O ₅	0.6376
SO ₃	PbSO ₄	3.788
Zn.....	ZnSO ₄	2.478
Zn.....	ZnO	1.2452
ZnSO ₄	ZnO	0.503

543. Table IV. Specific Gravities Corresponding to Degrees Baume for Liquids Lighter than Water.

Degrees Baume.	Specific gravity.	Degrees Baume.	Specific gravity.
10	1.000	37	0.843
11	0.993	38	0.838
12	0.986	39	0.833
13	0.979	40	0.829
14	0.973	41	0.824
15	0.967	42	0.819
16	0.960	43	0.815
17	0.954	44	0.810
18	0.948	45	0.806
19	0.942	46	0.801
20	0.935	47	0.797
21	0.929	48	0.792
22	0.924	49	0.788
23	0.918	50	0.784
24	0.912	51	0.781
25	0.906	52	0.776
26	0.901	53	0.771
27	0.895	54	0.769
28	0.889	55	0.763
29	0.884	56	0.759
30	0.879	57	0.755
31	0.873	58	0.751
32	0.868	59	0.748
33	0.863	60	0.744
34	0.858	61	0.740
35	0.853	62	0.736
36	0.848		

544. Table V. Specific Gravities Corresponding to Degrees Baume for Liquids Heavier than Water.

Degrees Baume.	Specific gravity.	Degrees Baume.	Specific gravity.
0	1.000	37	1.337
1	1.007	38	1.349
2	1.014	39	1.361
3	1.020	40	1.375
4	1.028	41	1.388
5	1.034	42	1.401
6	1.041	43	1.414
7	1.049	44	1.428
8	1.057	45	1.442
9	1.064	46	1.456
10	1.072	47	1.470
11	1.080	48	1.485
12	1.088	49	1.500
13	1.096	50	1.515
14	1.104	51	1.531
15	1.113	52	1.546
16	1.121	53	1.562
17	1.130	54	1.578
18	1.138	55	1.596
19	1.147	56	1.615
20	1.157	57	1.634
21	1.166	58	1.653
22	1.176	59	1.671
23	1.185	60	1.690
24	1.195	61	1.709
25	1.205	62	1.729
26	1.215	63	1.750
27	1.225	64	1.771
28	1.235	65	1.793
29	1.245	66	1.815
30	1.256	67	1.839
31	1.267	68	1.864
32	1.278	69	1.885
33	1.289	70	1.909
34	1.300	71	1.935
35	1.312	72	1.960
36	1.324		

545. Table VI. Relation of Baume Degrees to Specific Gravity, and the Weight per United States Gallon at 15.5° C.

Baume.	Specific gravity.	Pounds in gallon.	Baume.	Specific gravity.	Pounds in gallon.	Baume.	Specific gravity.	Pounds in gallon.
10	1.0000	8.33	38	0.8333	6.94	66	0.7142	5.95
11	0.9929	8.27	39	0.8284	6.90	67	0.7106	5.92
12	0.9859	8.21	40	0.8235	6.86	68	0.7070	5.89
13	0.9790	8.16	41	0.8187	6.82	69	0.7035	5.86
14	0.9722	8.10	42	0.8139	6.78	70	0.7000	5.83
15	0.9655	8.04	43	0.8092	6.74	71	0.6965	5.80
16	0.9589	7.99	44	0.8045	6.70	72	0.6930	5.78
17	0.9523	7.93	45	0.8000	6.66	73	0.6896	5.75
18	0.9459	7.88	46	0.7954	6.63	74	0.6863	5.72
19	0.9395	7.83	47	0.7909	6.59	75	0.6829	5.69
20	0.9333	7.78	48	0.7865	6.55	76	0.6796	5.66
21	0.9271	7.72	49	0.7821	6.52	77	0.6763	5.63
22	0.9210	7.67	50	0.7777	6.48	78	0.6730	5.60
23	0.9150	7.62	51	0.7734	6.44	79	0.6698	5.58
24	0.9090	7.57	52	0.7692	6.41	80	0.6666	5.55
25	0.9032	7.53	53	0.7650	6.37	81	0.6635	5.52
26	0.8974	7.48	54	0.7608	6.34	82	0.6604	5.50
27	0.8917	7.43	55	0.7567	6.30	83	0.6573	5.48
28	0.8860	7.38	56	0.7526	6.27	84	0.6542	5.45
29	0.8805	7.34	57	0.7486	6.24	85	0.6511	5.42
30	0.8750	7.29	58	0.7446	6.20	86	0.6481	5.40
31	0.8695	7.24	59	0.7407	6.17	87	0.6451	5.38
32	0.8641	7.20	60	0.7368	6.14	88	0.6422	5.36
33	0.8588	7.15	61	0.7329	6.11	89	0.6392	5.33
34	0.8536	7.11	62	0.7290	6.07	90	0.6363	5.30
35	0.8484	7.07	63	0.7253	6.04	95	0.6222	5.18
36	0.8433	7.03	64	0.7216	6.01
37	0.8383	6.98	65	0.7179	5.98

546. Table VII. Specific Gravity of Acetic Acid, Temperature 15° C.

Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.
100	1.0553	75	1.0746	50	1.0615	25	1.0350
99	1.0580	74	1.0744	49	1.0607	24	1.0337
98	1.0604	73	1.0742	48	1.0598	23	1.0324
97	1.0625	72	1.0740	47	1.0589	22	1.0311
96	1.0644	71	1.0737	46	1.0580	21	1.0298
95	1.0660	70	1.0733	45	1.0571	20	1.0284
94	1.0674	69	1.0729	44	1.0562	19	1.0270
93	1.0686	68	1.0725	43	1.0552	18	1.0256
92	1.0696	67	1.0721	42	1.0543	17	1.0242
91	1.0705	66	1.0717	41	1.0533	16	1.0228
90	1.0713	65	1.0712	40	1.0523	15	1.0214
89	1.0720	64	1.0700	39	1.0513	14	1.0201
88	1.0726	63	1.0702	38	1.0502	13	1.0185
87	1.0731	62	1.0697	37	1.0492	12	1.0171
86	1.0736	61	1.0691	36	1.0481	11	1.0157
85	1.0739	60	1.0685	35	1.0470	10	1.0142
84	1.0742	59	1.0679	34	1.0459	9	1.0127
83	1.0744	58	1.0673	33	1.0447	8	1.0113
82	1.0746	57	1.0666	32	1.0436	7	1.0098
81	1.0747	56	1.0660	31	1.0424	6	1.0083
80	1.0748	55	1.0653	30	1.0412	5	1.0067
79	1.0748	54	1.0646	29	1.0400	4	1.0052
78	1.0748	53	1.0638	28	1.0388	3	1.0037
77	1.0748	52	1.0631	27	1.0375	2	1.0022
76	1.0747	51	1.0623	26	1.0363	1	1.0007

547. Table VIII. Specific Gravity of Nitric Acid.

Specific gravity.	De-grees B.	100 pts. contain grms. HNO ₃ .	Specific gravity.	De-grees B.	100 pts. contain grms. HNO ₃ .
1.007	1	1.5	1.231	27	37.0
1.014	2	2.6	1.242	28	38.6
1.022	3	4.0	1.252	29	40.2
1.029	4	5.1	1.261	30	41.5
1.036	5	6.3	1.275	31	43.5
1.044	6	7.6	1.286	32	45.0
1.052	7	9.0	1.298	33	47.1
1.060	8	10.2	1.309	34	48.6
1.067	9	11.4	1.321	35	50.7
1.075	10	12.7	1.334	36	52.9
1.083	11	14.0	1.346	37	55.0
1.091	12	15.3	1.359	38	57.3
1.100	13	16.8	1.372	39	59.6
1.108	14	18.0	1.384	40	61.7
1.116	15	19.4	1.398	41	64.5
1.125	16	20.8	1.412	42	67.5
1.134	17	22.2	1.426	43	70.6
1.143	18	23.6	1.440	44	74.4
1.152	19	24.9	1.454	45	78.4
1.161	20	26.6	1.470	46	83.0
1.171	21	27.8	1.485	47	87.1
1.180	22	29.2	1.501	48	92.6
1.190	23	30.7	1.516	49	96.0
1.199	24	32.1	1.524	49.5	98.0
1.210	25	33.8	1.530	49.9	100.0
1.221	26	35.5			

548. Table IX. Specific Gravity of Hydrochloric Acid.

Percentage by weight at 15°.5C. compared with water at 4°C.

(Lunge & Marchlewski.)

Specific gravity.	Percent- tage HCl.	Specific gravity.	Percent- age HCl.	Specific gravity.	Percent- age HCl.
1.000	0.16	1.070	14.17	1.140	27.66
1.005	1.15	1.075	15.16	1.145	28.61
1.010	2.14	1.080	16.15	1.150	29.57
1.015	3.12	1.085	17.13	1.155	30.55
1.020	4.13	1.090	18.11	1.160	31.52
1.025	5.15	1.095	19.06	1.165	32.49
1.030	6.15	1.100	20.01	1.170	33.46
1.035	7.15	1.105	20.97	1.175	34.42
1.040	8.16	1.110	21.92	1.180	35.39
1.045	9.16	1.115	22.86	1.185	36.31
1.050	10.17	1.120	23.82	1.190	37.23
1.055	11.18	1.125	24.78	1.195	38.16
1.060	12.19	1.130	25.75	1.200	39.11
1.065	13.19	1.135	26.70		

49. Table X. Sulphuric Acid.

Percentage by weight of H_2SO_4 at $15^\circ.5\text{C}$.

(Lung and Isler.)

Specific gravity.	Percentage of H_2SO_4 .	Specific gravity.	Percentage of H_2SO_4 .	Specific gravity.	Percentage of H_2SO_4 .
1.005	0.83	1.200	27.32	1.395	49.59
1.010	1.57	1.205	27.95	1.400	50.11
1.015	2.30	1.210	28.58	1.405	50.63
1.020	3.03	1.215	29.21	1.410	51.15
1.025	3.76	1.220	29.84	1.415	51.66
1.030	4.49	1.225	30.48	1.420	52.15
1.035	5.23	1.230	31.11	1.425	52.63
1.040	5.96	1.235	31.70	1.430	53.11
1.045	6.67	1.240	32.28	1.435	53.59
1.050	7.37	1.245	32.86	1.440	54.07
1.055	8.07	1.250	33.43	1.445	54.55
1.060	8.77	1.255	34.00	1.450	55.03
1.065	9.47	1.260	34.57	1.455	55.50
1.070	10.19	1.265	35.14	1.460	55.97
1.075	10.90	1.270	35.71	1.465	56.43
1.080	11.60	1.275	36.29	1.470	56.90
1.085	12.30	1.280	36.87	1.475	57.37
1.090	12.99	1.285	37.45	1.480	57.83
1.095	13.67	1.290	38.03	1.485	58.28
1.100	14.35	1.295	38.61	1.490	58.74
1.105	15.03	1.300	39.19	1.495	59.22
1.110	15.71	1.305	39.77	1.500	59.70
1.115	16.36	1.310	40.35	1.505	60.18
1.120	17.01	1.315	40.93	1.510	60.65
1.125	17.66	1.320	41.50	1.515	61.12
1.130	18.31	1.325	42.08	1.520	61.59
1.135	18.96	1.330	42.66	1.525	62.06
1.140	19.61	1.335	43.20	1.530	62.53
1.145	20.26	1.340	43.74	1.535	63.00
1.150	20.91	1.345	44.28	1.540	63.43
1.155	21.55	1.350	44.82	1.545	63.85
1.160	22.19	1.355	45.35	1.550	64.26
1.165	22.83	1.360	45.88	1.555	64.67
1.170	23.47	1.365	46.41	1.560	65.08
1.175	24.12	1.370	46.94	1.565	65.49
1.180	24.76	1.375	47.47	1.570	65.90
1.185	25.40	1.380	48.00	1.575	66.30
1.190	26.04	1.385	48.53	1.580	66.71
1.195	26.68	1.390	49.06	1.585	67.13

Table X (Continued).

Specific gravity.	Percentage of H ₂ SO ₄ .	Specific gravity.	Percentage of H ₂ SO ₄ .	Specific gravity.	Percentage of H ₂ SO ₄ .
1.590	67.59	1.720	78.92	1.825	91.00
1.595	68.05	1.725	79.36	1.826	91.25
1.600	68.51	1.730	79.80	1.827	91.50
1.605	68.97	1.735	80.24	1.828	91.70
1.610	69.43	1.740	80.68	1.829	91.90
1.615	69.89	1.745	81.12	1.830	92.10
1.620	70.32	1.750	81.56	1.831	92.30
1.625	70.74	1.755	82.00	1.832	92.52
1.630	71.16	1.760	82.44	1.833	92.75
1.635	71.57	1.765	82.88	1.834	93.05
1.640	71.99	1.770	83.32	1.835	93.43
1.645	72.40	1.775	83.90	1.836	93.80
1.650	72.87	1.780	84.50	1.837	94.20
1.655	73.23	1.785	85.10	1.838	94.60
1.660	73.64	1.790	85.70	1.839	95.00
1.665	74.07	1.795	86.30	1.840	95.60
1.670	74.51	1.800	86.90	1.8405	95.95
1.675	74.97	1.805	87.60	1.8410	97.00
1.680	75.42	1.810	88.30	1.8415	97.70
1.685	75.86	1.815	89.05	1.8410	98.20
1.690	76.30	1.820	90.05	1.8405	98.70
1.695	76.73	1.821	90.20	1.8400	99.20
1.700	77.17	1.822	90.40	1.8395	99.45
1.705	77.60	1.823	90.60	1.8390	99.70
1.710	78.04	1.824	90.80	1.8385	99.95
1.715	78.48				

550. Measures, Weights and Temperatures.

One Imperial gallon	=	277.27 cubic inches.
One wine gallon	=	231.0 cubic inches.
One wine gallon	=	3.7854 liters.
One wine gallon	=	8.3389 pounds water at 4° C.
One quart	=	57.88 cubic inches.
One quart	=	.9464 liter.
One liter	=	1.0567 quart.
One cubic foot	=	28,315 cubic centimeters.
One cubic inch	=	16.38 cubic centimeters.
One cubic centimeter	=	.061 cubic inch.
One pound Avoirdupois	=	453.6 grams.
One ounce Avoirdupois	=	28.35 grams.
One gram	=	15.432 grains.
One inch	=	.0254 meter.
One foot	=	.3048 meter.
One yard	=	.91438 meter.
One meter	=	39.3708 inches.

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