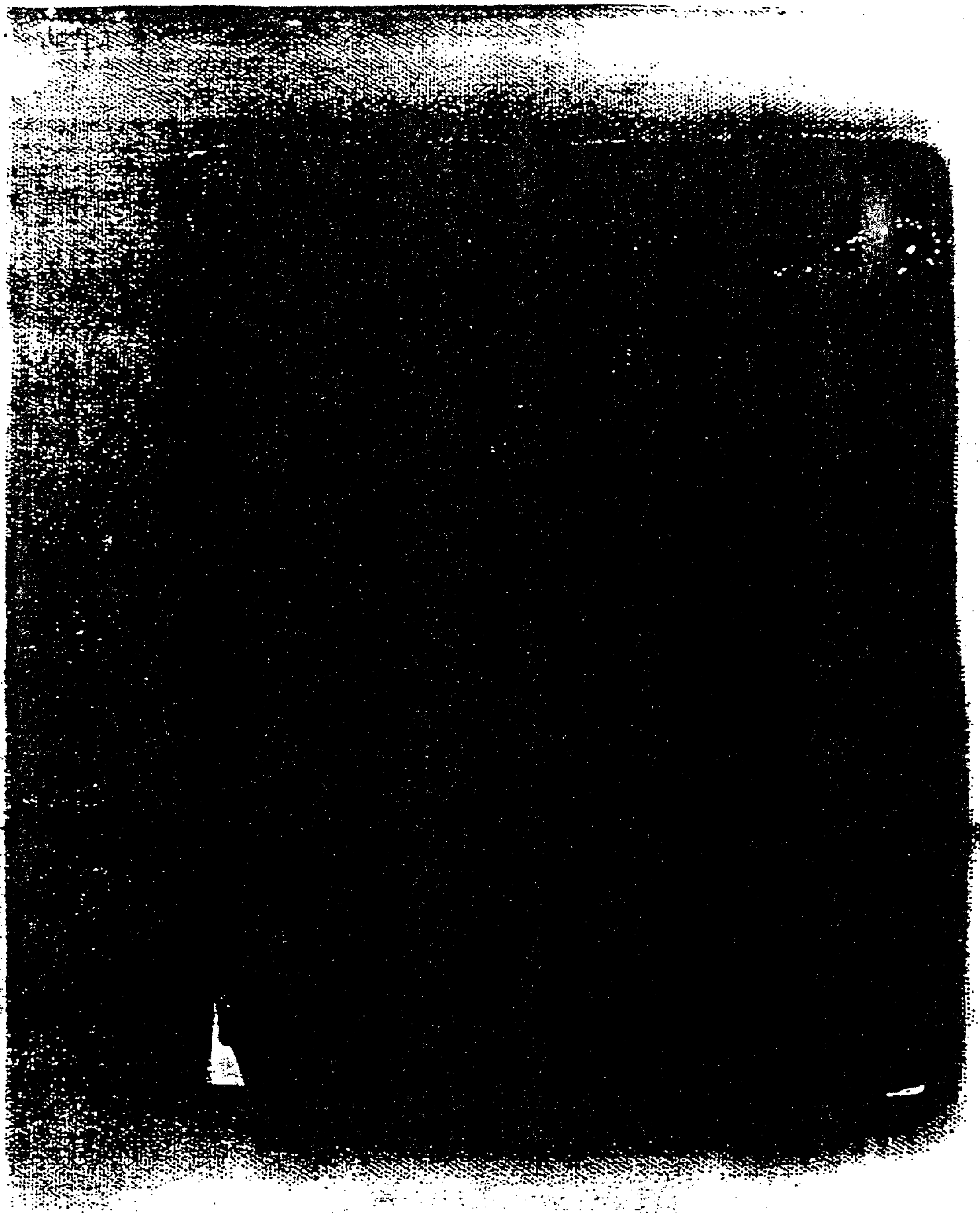

CRUDE MATERIAL
for
THE PAINT MANUFACTURER

A Treatise Written Especially for the Salesmen of the ACME WHITE LEAD AND COLOR WORKS, *Detroit, Michigan*

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0007-SWP-000007262

they attach themselves to rocks, ships' bottoms, etc., and it is to prevent this attachment that anti-fouling compositions are used. The salt of sea-water is a chloride; and if the paint used contains mercury, a chloride of mercury is formed; if copper, an oxy-chloride of copper, and so on. As a matter of fact, all metallic salts capable of forming chlorides in combination with the salt and oxygen in sea water are anti-fouling. The only difficulty is to get the right percentage of the metallic salt.

If any albuminous substance comes in contact with these chlorides, it instantly coagulates and if there is any part of marine life, which on contact with this class of paint would act in a similar manner, it could not, of course, attach itself to a ship's bottom. This, as we understand it, is the real explanation why anti-fouling paint is effective, for it is well known that on the anterior end of the head of this cirrepedia there is an albuminous and cement-like substance which is affected, as stated, by contact with the poisonous salt.

WHITES

We will now consider the paint pigments which are commonly and properly classified as crude material, and divide them into groups, as Whites, Blacks, Browns, Blues, Greens, Yellows, and Reds. The principal whites, are conceded to be zinc and lead—oxide of zinc and carbonate of lead. Both are so generally well known, that it seems superfluous to do more than refer to them, but this booklet would be incomplete without, at least, a cursory description.

CARBONATE OF LEAD

The term "carbonate" of lead is not strictly correct, as a carbonate by itself would be too crystalline in its structure to be of use for paint. In composition, it is both carbonate and hydrate, or hydroxide, and for a perfect product it must be combined in definite proportions. The recognized chemical formula is $2\ Pb\ CO_3\ Pb\ H_2O_2$ (two molecules of carbonate to one molecule of hydrate, representing 70 and 30 per cent respectively). If much more hydrate than this, the opacity is reduced (requires more thinner), and if much more carbonate, the binding and working property is impaired; it is difficult to break up, covers poorly and chalks rapidly. However, a composition of 75 per cent carbonate and 25 per cent hydrate makes a good workable lead, more especially if of reasonable age—say six months. Under favorable circumstances, one hundred pounds of the metal will yield eight-five pounds of corroded lead, but the general run is about seventy-five. The metallic or blue lead must be pure—not only desilverized, but be free from all other metals—zinc, bismuth, copper, etc. If there is a trace of silver, the product will have a pink cast, and a very small amount of iron would give it a brownish tint.

OLD DUTCH PROCESS

The term "old dutch process," as applied to the corrosion of metallic lead is well known and explains itself, but it may be said that the excellence of the product is largely due to careful and intelligent handling. The metal is dissolved at a low heat in kettles and is discharged into a box by an endless chain which carries perforated circular discs, technically called "buckles." These buckles may be ⅛ or ¼-inch thick and weigh up to one pound. The corrosion, as you know, takes place in stacks and the requisite heat, etc., is generated by spent tan bark. The acetic acid as purchased is the commercial article, generally known as No. 8, which contains 28 to 30 per cent of glacial acid (the standard) which is reduced to the required strength, each manufacturer having his own "rule of thumb" to determine just what that is. The method of procedure is to lay the buckles on the inner projecting parts of the acid crocks (which are much like flower pots in appearance) so that the metal does not come in actual contact with the vinegar. On the top of a row of crocks boards are laid and on these boards the tan bark is spread. Then a new layer of crocks is placed and covered the same way, and so on until the stack is full, the walls being filled in with old tan bark to help decompose the new in the beds. The heat of the tan bark generates carbon dioxide and volatilizes the acid, which attacks the buckle from the outside and gradually eats inward. The buckles swell upwards, so that when taken out, they are frequently twice their original thickness.

A certain heat must be maintained in the stack, or much of the metal will be uncorroded, and if there is an excess of heat, the product will be yellowish. Ventilation is secured by a square hollow shaft which is carried up from each layer to the top of the stack. The confinement of the metal within certain limits during corrosion makes a definite molecular structure impossible, and the product is amorphous. The stacks are opened at the expiration of ninety or one hundred days and the lead taken from the crocks. It is then seen that only a certain percentage of the blue lead has been fully corroded, and separation is necessary. This is accomplished by means of a "separator," a description of which is unnecessary. It does the work effectively and the uncorroded part is either sent back to the stacks or is subjected to calcination in furnaces for oxides of lead. The final processes are screening, washing free of acid, grinding in water, floating in tanks, and drying in copper pans for its ultimate grinding in oil.

Any lead imperfectly ground in the water will fail to float. This is known as the "core" and is usually calcined for the better class of orange mineral.

THE "PULP" PROCESS

The "pulp" process, about which so much has been said, is simply this: When the lead has passed through the last floating trough, it goes into an upright tank fitted with mixers, which are started up and the oil added. The mixing continues until the oil is thoroughly incorporated and the water expelled. The lead is then run into kegs without grinding. A small per cent of the water certainly remains. There are many reasons which we could name, why this process should be condemned, but so far as we know, it is not now generally in use. It probably was originated from humanitarian, rather than economic motives, for there is no disguising the fact that the removal of the bone-dry lead from the pans is a dangerous work for employees.

In speaking of Old Dutch Process we are accustomed to think that Corrosion of Metallic lead by Acetic Acid originated with the Dutch, but this is not the case. The principle is not less than two thousand years old, although of course methods were very crude. We know for a certainty that Earthern Crocks were used before the Christian Era. At least we have it on the authority of Theophrastus (and no doubt of others) who explains that thin pieces of metal were placed in such vessels containing vinegar and that the corroded part was removed at intervals, etc.

QUICK PROCESS Now if it is considered necessary to mould pig lead in small buckles to facilitate corrosion, it stands to reason that other methods whereby the metal is run into ribbons, or blown in a fine spray, cobweb-like, etc., will reduce the time very considerably, and so we have what is commonly spoken of as "quick process," the most conspicuous of which is probably the "Carter Co.'s" who disintegrate the melted lead into small particles by steam blast and accomplish corrosion in chambers. All quick process leads in fact are made in chambers or rooms, as distinguished from stacks, but the same elements are required for corrosion, and the nearer the product approximates to a perfectly made old dutch process lead, the better it will be.

The three indispensables are acetic acid, carbon dioxide and moisture. Pure lead paint will last just as long as the oil binder and no longer. When that is gone, the lead flours. There is no getting around this fact! We grind lead only to thoroughly incorporate the oil. If not made fine before drying, it can never be ground fine. Too much milling destroys its opacity. As white lead is easily affected by sulphur, it is evident that no pigment containing sulphur should be mixed with it or used for tinting.

FLAKE WHITE

There are several other carbonates of lead made by either the wet or dry process, but none of them are of much interest to the paint manufacturer, excepting the carbonates which you know, as Flake White, mostly imported from England and Krems or Kremnitz White from Germany. An essential difference between Flake White and American white lead is in the metal itself. English lead is cast in thin strips about a yard long and four and a half inches wide. Corrosion takes place in chambers, being carefully regulated, and under full control all the time, which is usually forty days.

KREMNITZ WHITE

The process for Kremnitz is dry precipitation and the substance to be corroded is not the metal, but the mon-oxide of lead (or litharge) which is mixed to a paste with acetic acid or the acetate of lead, placed on shelves, and carbonic acid turned in. In all the subsequent operations after corrosion, extreme care is necessary and the water must be pure. Both the Flake and Kremnitz White is higher in carbonate than ordinary white leads and is more buoyant, the former being largely used to body zinc for enamels, and both of them for grinding, as coach colors.

SULPHATE OF LEAD

The sulphate of lead is a practically unchangeable white of good color and is used for some purposes, but rarely, if ever, ground for a white lead. This pigment can be precipitated from a solution of basic lead acetate (litharge dissolved in hot acetic acid) by sulphuric acid. In this way, about 350 pounds of the oxide requires 160 pounds of the sulphuric acid, which gives a yield of nearly 500 pounds sulphate of lead. The stronger acid combining, releases the weaker, so that the acetic acid is washed away and lost.

SUBLIMED LEAD

Although the sulphate is not in general use, the pigment known as sublimed has a considerable sale. The principle upon which this article is produced may be briefly and yet comprehensively explained as follows:

When lead ore (Galena, or native lead sulphide) is heated in a furnace with access of air, it oxidizes partly to lead oxide and partly to sulphate of lead, the amount of oxide depending on the amount of air which comes in contact with the lead ore. If this is small, then sulphate is mostly formed. If high, there is likely to be a decomposition to oxide and sulphur dioxide. The proper definition of the product is oxy-sulphate of lead. It contains varying proportions of zinc, because lead and zinc ores are intimately associated and it is exceedingly difficult to wholly separate them. As a finished product, it is very white and fine and takes more oil than dutch process carbonate. From its nature, it is impervious to gases, and so retains its purity of color under almost all circumstances.

STANDARD ZINC-LEAD

Another interesting White made direct from the ore by fire process is Standard Zinc-Lead, whose home is in Canon City, Col. It gets the name "Standard" from the fact that it is standardized in composition and color. As perfected, it is a molecular combination of zinc oxide, lead sulphate, and small proportions of lead carbonate and oxide. We speak of it approximately as 50 per cent lead, and 50 per cent zinc, the combination being effected at a high temperature while the metals are in form of vapor. The union is far more intimate than could be attained by mechanical mixing of the two pigments, and it is this quality which gives it a peculiar and distinctive value.

"Containing no hydrated or unstable salts, it is not affected by sulphuretted hydrogen or other sulphurous derivatives, and all its components being chemically stable, it has no injurious effect upon the oil with which it is combined. On this account, paints containing it show no tendency to chalk, peel, or become transparent. For the same reason, also, it may be tinted with chemical or other colors without inducing chemical color changes. Thus, vermillion, ultramarine, and other sulphur bearing pigments may be mixed with it without risk."

The process of manufacturing, as explained by the makers, "begins with the analysis of the ores

PROCESS OF MANUFACTURE

to ascertain their proportional content of metallic zinc and lead. They are then crushed and screened by suitable machinery, and the comminuted materials are mixed, also by machinery, in proportions that will yield the proper relative proportions of zinc and lead compounds in the product. The ore is now ready for charging, together with a sufficient quantity of fine coal to maintain combustion, into the volatilizing and oxiding furnaces.

"These furnaces, devised specially for the purpose, 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 are reduced to the metallic state and converted to other volatile forms, but on reaching these conditions are instantly vaporized and drawn by means of exhaust fans into combustion chambers, where the chemical transformation of the product, due to oxidization, completes itself.

"Thence the white fume passes forwards through a series of long cooling flues to suspended woolen collecting bags, whence the waste gases of combustion escape, while the pigment is retained.

"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, condensed in bulk, desulphurized and whitened to the standard color. Finally, the finished product is bolted through fine cloth on vibrating screening appliances and then packed automatically for shipment."

OXIDE OF ZINC

Oxide of zinc is now used in enormous quantities, and the better it is known, the more its good qualities are intelligently developed. As a corrective for the drawbacks of white lead, it is invaluable, and for interior use and very many special purposes in the enamel line and dipping process, it is indispensable. Like most other pigments, it has a few faults, but paint manufacturers are conversant with and know how to overcome them. The best of this class comes from France and is known as Vielle Montagne Red and Green Seal, the latter being the better quality and higher priced. The Antwerp Red and Green Seal is sold for less money and is not considered as good as the Paris. The New Jersey Zinc Co. follows closely with their "Florence" (named after Florence, Pa., where it is made) Red and Green Seal, which is made by the same process—from the metal and not from the ore.

HOW MADE

The metallic zinc is melted in retorts and distilled over into a chamber where it meets a current of air which oxidizes it, after which it is freed from its impurities by special treatment. The ordinary American zinc oxides are

AMERICAN ZINCS

produced by burning in furnaces, made of iron and brick, with fire-brick lining, a mixture of fine coal and zinc ore. From this calcination, a vapor arises, which, coming in contact with air, forms itself into the white powder, with which you are familiar. The furnaces are heated and the grates covered with a layer of fine anthracite coal which is ignited. When the coal is burning brightly, the charge of ore and coal, and sometimes limestone, is thrown on it, the blast is turned on gradually and after half or three-quarters of an hour, the charge is hot enough to reduce and distill some zinc which burns to oxide with a green flame at the opening at the top of the furnace; when the zinc flame shows, the damper in the pipe leading to the collecting apparatus is opened and the oxide is allowed to go over. This damper is kept closed while charging the furnace to prevent any coal or ore dust from being carried over the oxide. When the furnace is hot enough to make oxide, the charge is partly melted and no dust can be drawn from it. The charge is occasionally raked, and the blast gradually increased, until nearly all of the zinc has been drawn off. The blast is then shut off, the damper in the pipe is closed, and the clinker remaining in the furnace is broken up and raked out, fresh coal is charged and the entire operation is repeated.

The gases and oxide of zinc from the furnaces are drawn by large fans through settling and cooling chambers (where the heavier impure oxide settles) and forced over to the bag rooms. These bag rooms are large buildings having a series of pipes at the top from which hang muslin bags about six feet in circumference and from twenty-five to forty feet long. The gases pass out through the bags, and the oxide is caught in them. The bags have to be shaken every hour or so to prevent their becoming clogged. The oxide is removed from the bag rooms every twelve or twenty-four hours and taken to the packing room. The bolting is through silk cloth, in machines similar to those used for flour, and packed in barrels ready for shipment.

The furnaces are built in blocks, each of which has its own blast fan, exhaust fan, carrying off pipes, settling chamber and bag room, so as to be entirely independent. A sample of the oxide of each block is taken each time the bags are emptied and tested for color and purity, and it is graded according to the result of these tests. The size of the lots tested varies in different works from three to six thousand pounds. In this way, we have "Selected," "XX," and so on. The chemical formula is about 80% zinc and 20% oxygen. It has one characteristic which no other white pigment has—it is soluble in dilute sulphuric acid. It mixes well with all other pigments without change and takes considerable oil to grind. The white that is commonly known as "Lithapone," "Ponolith," "Beckton White," and other registered names, is also a zinc—a sulphide. Many years ago, it was imported from England under the name of "Charlton White," and owing to its good covering power, it was quite extensively used in combination for prepared house paint. There was difficulty, however, in maintaining a uniform product and continuous supply. This, with trouble in the manipulation, killed it and only during the past few years has it been restored to a certain measure of favor, but it is now rarely used for mixed paint. The manufacture in this country is confined to two or three firms, and most of the importation is from Germany. It requires expert knowledge to handle it properly, and for obvious reasons, it should be used only for interior work, although it is claimed for some brands, that it will stand exposure without change. Broadly speaking, it is a combination of sulphate of barium and sulphide of zinc, precipitated together. It is conceded that for paint purposes it should carry not less than 30% of the zinc sulphide which is equivalent to the imported Red Seal. The Green Seal has (or should have) 35% to 40%; the Blue Seal, about 22%; and the Yellow Seal, only 15%. The process of making is more or less of a secret,

LITHAPHONE

but a solution of zinc chloride is prepared, to which is added sulphide of barium, and finally a solution of sulphate of soda; after which, it is washed and ignited in a current of air, to a red heat maintained for two hours or less. For cheaper goods, after the above solutions are mixed, a solution of barium chloride is added, and followed by another solution of sulphate of soda, so that the precipitate will contain more sulphate of barium.

BARYTES

Among those who are not well informed, it is common to hear disparaging remarks about "barytes," the idea being that its only mission is that of a cheapener, but this is a grave mistake. Very few paint firms would be able to do business without this valuable article. Nor is it the low-priced pigment so frequently thought. In some of its forms, it is quite expensive, approximating very nearly, for instance, to zinc oxide. When it is understood that barytes (which is chemically known as sulphate of barium) is perfectly inert and not susceptible to gases or the most powerful of acids, some idea of its importance can be imagined. When a chemist treats a little of this powder in a test tube and finds the barium reaction, he is apt to conclude that he has secured the ordinary barytes of commerce, but it is quite likely that it may be an article costing three times as much. For very many purposes, it is necessary to use