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AN ELECTROLYTIC PROCESS FOR THE MANUFACTURE OF WHITE LEAD.[1]

BY R. P. WILLIAMS.

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WHITE LEAD is the basis *par excellence* of white paint. For hundreds of years it has been used, mixed with linseed oil, as the main pigment where permanent, opaque, white color is desired.

Up to the present time there have been but two radically different processes of manufacture that have proved in any degree successful. These are known as the Dutch and the French processes. The English and the German are only modifications of the same principle as the others. The Dutch process is the only really successful one. I do not propose to go into the details of either of these processes, since they are well known to every chemist, but only to recall just enough of them to serve as the basis of comparison and as an introduction to the one I am to describe. Both the French and the Dutch, as well as the many modifications of them, depend upon one compound; *viz.*, lead acetate (or better, sub-acetate). This is the compound which has always been regarded as the essential first step in white lead manufacture. The fact is interesting, since white lead as a pigment has been known for more than 2,000 years, and from the earliest times it has been made by the action of acetic acid on lead. The name, Dutch process, is a

[1] Read at the Springfield meeting.

misnomer, as the process was introduced by the Dutch or Flemish people over 300 years ago from Italy, where it had been employed for hundreds of years previously. In fact, Pliny in the first century describes the essentials of the process, and it is said to have been employed in his country ever since his time, though, of course, on an extremely limited scale at first. Indeed Theophrastus, about 300 B. C., describes the preparation of a white pigment from lead and vinegar. This may have been the acetate, or it may have been the carbonate. The new process is a radical departure from all the old ones in not employing acetic acid at all, but in acting upon lead with nitric acid, which is generated by electricity.

The process consists of four reactions, as given below. First, the electrical preparation of nitric acid and sodium hydroxide. Second, the action of the nitric acid on lead, forming lead nitrate. Third, the reaction of lead nitrate and sodium hydroxide to form lead hydroxide. Fourth, the combination of lead hydroxide and sodium bicarbonate to form lead carbonate.

In the first step of the process, a solution of sodium nitrate is decomposed by an electric current from a dynamo. The strength of solution required is not important, 10° Baumé, or say one pound to the gallon, being sufficient. This solution is put into a series of cells, constructed of wood, and divided into two compartments by a porous partition. At the plus electrode is fastened a pig of lead, and at the minus a sheet of copper. The solution being run in from an overhead reservoir, and the current turned on, the nitrate is decomposed according to equation (1), nitric acid collecting at the plus electrode and sodium hydroxide at the minus. The nitric acid at once attacks the lead and forms lead nitrate, which dissolves, equation (2), whereas the sodium hydroxide produces no effect on the copper at the negative pole. Finally the lead nitrate solution and the sodium hydroxide solution are drawn off separately, and mixed as desired, in quantitative proportions, in a receptacle. The result as shown in equation (3), gives lead hydroxide as a white, amorphous precipitate, and leaves sodium nitrate in solution. This is practically the original nitrate, and its regeneration shows one of the economic excellencies of the process, for the nitrate can be used over and over again, as the source of more acid.

It has been found at the experiment station, that but little additional sodium nitrate is required for a repetition of the process as complete as the original. The lead hydroxide is then filtered from the sodium nitrate. This is done automatically and continuously, by a rotary filtering device, and the sodium nitrate is pumped back into the original reservoir. The fourth step is, in some respects, the most interesting of all, and consists in adding to the lead hydroxide a solution of sodium bicarbonate (or of the normal carbonate). Reaction (4) at once takes place. It will be noted that sodium hydroxide is the product in solution, and lead carbonate the precipitate. Another beauty of this process is that the sodium hydroxide removes most of the impurities, if there are any, in the lead hydroxide; for instance, it will dissolve any salts of aluminum or of zinc, and it removes organic matter.

These impurities appear in the solution, leaving the precipitate remarkably white. Once more, this by-product, sodium hydroxide, by passing carbon dioxide into it, is converted into bicarbonate and the latter can be used again. Thus the main agent in each of the two principal steps, sodium nitrate and sodium bicarbonate, is made to do duty over and over again, with but slight additions.

$$(1)\ NaNO_3 + H_2O = Na\overset{-}{O}H + H\overset{+}{N}O_3.$$
$$(2)\ 2HNO_3 + Pb = Pb(NO_3)_2 + H_2.$$
$$(3)\ Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3.$$
$$(4)\ Pb(OH)_2 + HNaCO_3 = PbCO_3 + NaOH + H_2O.$$

It is doubtful whether (1) and (2) take place as above, but probably the reaction is as follows, since hydrogen is liberated at the minus electrode:

$$2NaNO_3 + 2H_2O + Pb = (2N\overset{-}{a}OH + H_2) + PbO_2\overset{+}{(}NO_2)_2.$$

Let us now turn from the theoretical to the practical part of the matter. The first question which naturally arises is, will this process so beautiful in theory, and as a laboratory experiment, work on a large scale and give sufficiently practical results to compete with the other methods of manufacture, and make it a lasting contribution to inventive science?

An experimental station was for several months in operation in Cambridge, Mass., erected and run under the direction of Mr. Arthur Benjamin Brown, the inventor of the process. This was capable of turning out some 500 pounds of white lead per day. Its success was regarded as beyond question. The cost of white lead by this process is more than covered by the gain in weight, and is but a fraction of the cost by the Dutch method. The reasons are, first, in the electrolytic process pig lead is used, as it comes from the smelting furnace. In the Dutch it has to be remelted, cast into "buckles" of definite size, and, after the action of acetic acid, from one-third to one-half is left uncorroded and has to be recast.

Second, the process is almost instantaneous, as every reaction takes place rapidly, while by the other mode from two to six months is required.

Third, in materials and labor there is great saving. No free acid is used, either acetic or nitric, and the agents sodium nitrate and bicarbonate, are used repeatedly. By the old method a plant covering a large area is filled for months with fermenting tan bark or manure, acetic acid and lead, while the process is going on, and at its completion, the product is removed with much labor, and has to be thoroughly and repeatedly washed to dissolve out any lead acetate remaining. It must be ground and reground under water, and even then is not likely to be of uniform texture. It is also a poisonous and dirty process. The electric method, being continuous, is complete the same day, requires but a very small force of men, as almost all the operations are automatic, and is a clean and non-poisonous process.

The texture of the product is almost molecular in fineness, as might be expected from its being produced by replacement in the hydroxide. Hence it needs no grinding. It is so fine as to remain suspended in water for a long time, and in order to filter it a special brand of cloth had to be made, as even filter-paper would scarcely retain it.

One of the most important practical questions is: How does paint made from electrolytic white lead compare with that made from Dutch lead in durability, opacity, and covering power? Specimens have been submitted to some of the largest dealers and painters in New England and elsewhere, and Mr. Brown, the inventor, has spent the last two years, aided by a competent corps of assistants, not only in the development of his new process, but in making thorough and systematic tests of the product. Inside and outside surfaces have been exposed to the severest extremes of weather, to the varied fumes of the laboratory, and to other crucial tests. Dutch paint and electrolytic paint have been exposed side by side for two years, and no difference can be detected in durability or opacity. The covering power of the new paint is considerably greater than that of the Dutch. Experiments vary as to the increased percentage from twelve to twenty, or even higher, but in no case was there found to be a smaller percentage.

What is the cause of such an increase? This leads us to discuss somewhat more fully the nature and composition of white lead made by the various processes. Dutch white lead consists approximately of two molecules of the carbonate to one of the hydroxide, $2PbCO_3.Pb(OH)_2$. This, however, appears not to be constant, as might be inferred from its mode of manufacture. Lead hydroxide is a white, amorphous substance. Lead carbonate is either a spongy transparent, globular powder, or is crystalline. Whether globular or crystalline depends upon its mode of preparation. Now certain properties of these two forms are quite different, and this difference explains the use of one and the disuse of the other form as a pigment. The globules of the one form are said to be from 0.00001 to 0.00004 of an inch in diameter. These, in the grinding of lead with linseed oil, are supposed to take up the oil, somewhat as a sponge absorbs water. The Dutch process lead is the globular variety, and to this fact has been attributed the greater body and permanence of the paint made from it than that made by most other processes. The crystalline variety of the carbonate is found not to absorb oil to anything like the same extent as the globular, no matter to what degree of fineness it is ground, the surface of the minute crystals being impervious. Half a century ago Thenard invented the "quick process lead." or "French process." This is now carried on in Clichy, France, and some other places, and sold as "Clichy White." It is made by dissolving litharge in acetic acid and then passing into the sub-acetate of lead solution formed, carbonic acid gas. Thus is formed neutral lead carbonate. It was at first thought to be a revolutionary process. but it soon became apparent that the product did not give the capacity or body, which Dutch lead gave, and of course it lacked permanence. Made in this way the carbonate is crystalline. Under the brush it is found not to cover as much surface and not to spread as well. or it is said to lack "body," although of the same composition as the other. Other rapid processes—and there have been hosts of them—have invariably met with no better success, for the reason that the carbonate formed is the crystalline instead of the globular variety. To this fact we may mainly attribute the long continued use of Dutch process lead. The committee of experts appointed by the British Home Secretary, visited forty-six works, and found only one using the precipitation process and three the chamber process. They say: "While some of the substitutes are cheaper to make, and far less poisonous, yet they are far from equalling the Dutch lead as a pigment. Neither can they recommend other process than the old Dutch process, for manufacturing the product."

Thus we see that until now, no cheaper method has been found for producing the globular variety. The electrolytic process *does* produce the globular kind. and a finer variety even than the Dutch, so fine in fact. that it was almost impossible to find a filter that would retain it. This probably accounts for the superiority of the electrolytic brand, as regards body and covering power over any other kind produced. Experiment shows that the pure carbonate will do as well as a mixture of carbonate and hydroxide. By the new process it is easy to make either the pure carbonate, or a mixture in any proportion, of carbonate and hydroxide. The practicability and cheapness of the electrolytic process, and the efficiency of the product being conceded, we may inquire lastly: What are the probabilities of this method being superseded by others in the future?

No other white pigment has yet been formed, or seems likely to be found, which will take the place of white lead. The two main substitutes are zinc white, ZnO, and permanent white, $BaSO_4$. But these do not stand the test with lead white, having far less capacity, and less covering power. Especially will they not compete with the cheapening of the latter by the new process. Hence, we must look to lead to give us the white pigment of the future.

Now what are the possible ways of making lead carbonate? There are but three common solvents of the metal; chlorine, acetic acid, nitric acid. Chlorine is at once ruled out for all practical purposes, for reasons that need not be mentioned here. Acetic acid seems to have been the substance universally employed to the present time, for getting the metals into a preliminary state for making the carbonate. As before noted, from the time of Theophrastus to the present day a host of persons in every age and many countries, have experimented and written upon the subject, all using the same method so far as concerns making lead acetate.

The inventor of the present process, worked a long time upon the acetate, but as acetic acid is an organic substance of quite complex structure, it broke up very readily under influence of an electric current, giving rise to unendurable fumes, and its use had to be abandoned. For these reasons it is safe to say that no electrolytic process is likely to employ the lead acetates. The only solvent left is therefore nitric acid. Free nitric is not likely to be used for three reasons: First, it could hardly be employed in electrolysis; Second, it would be more expensive than Chile saltpeter; Third, its reaction with lead would give rise to noxious nitric oxide fumes, and its by-product would not be re-usable. It should be said that no gases except hydrogen arise in the electrolytic process, in which the acid, as fast as liberated, combines with the lead, as may be seen from equation (2).

Now the only feasible source of nitric acid yet found, is either sodium or potassium nitrate. The former being far the more abundant and cheaper, is here as elsewhere employed, as a source of the acid, and no other nitrates are found to any extent in nature.

It would seem from what has been set forth, that not only is the process above described the most valuable and revolutionary ever invented for the manufacture of white lead, but that there is not a probability of any other process taking its place, in the near future.

This new process was invented in 1892, by Arthur Benjamin Brown, a chemist and mining engineer of Boston. It is to-day for the first time made public. The reason this has not before been done is because time was necessary to complete many details for production on a large scale, and to secure requisite patents. These are now completed, and a large company is organized to put the process into practical operation. I propose for this invention the name—The Brown Electrolytic Process.

THE CHLORIDES OF ZIRCONIUM.[1]

By F. P. Venable.

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In a report upon the examination of the chlorides of zirconium[2] it was stated that pure zirconium tetrachloride was formed by the solution of zirconium hydroxide in hydrochloric acid and repeated crystallization from the concentrated acid. This statement was based on a partial analysis by Linnemann[3] the result of which made him call the substance the tetrachloride; and on repeated partial analyses of my own in which the zirconium present was determined by ignition as zirconium dioxide. So firmly convinced was I of the fact that this was the normal tetrachloride that I determined to use it in revising the atomic weight. Ten closely agreeing determinations were made and they yielded as the percentage of zirconium dioxide found 52.99, or, calculating with 90.62 as atomic weight of zirconium (Bailey) 39.16 per cent. of zirconium. The zirconium in the tetrachloride amounts to 38.99 per cent.

Bailey made several very widely differing determinations of the chlorine in this body and considered it the oxychloride. His determinations varied so greatly and his mode of drying were so faulty that I simply concluded he was mistaken, being

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[1] Read at the Springfield meeting.

[2] *J. Am. Chem. Soc.*, *1894*, 16, 460–475.

[3] Lond. Chem. News, 52, 233–240.