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SATIN WHITE AND METHOD OF MAKING THE SAME

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This invention relates to improvements in a product of the type commonly designated "satin white" and also to improvements in the method of producing the same. More particularly, the improved product is an intimate, coprecipitated mixture of satin white and calcium sulfite, the satin white largely predominating. While the precise, chemical nature of the product has not been definitely determined it is possible that it is a chemical combination of satin white and calcium sulfite.

This application is a continuation-in-part of my pending application, Ser. No. 351,113, filed August 3, 1940.

The precise character of satin white has been subject to some discussion among chemists. It is now generally accepted, however, that this product, which is usually formed by the reaction of a concentrated solution of iron-free alum with milk of lime, is calcium sulfo-aluminate and may be represented by the formula:

$$3CaO.Al_2O_3.3CaSO_4.31H_2O.$$

In the ordinary procedure for the production of satin white, care must be exercised to eliminate the usual iron content from the alum employed, otherwise the resulting product will be discolored. The ferric hydroxide formed in the reaction will impart a yellowish or other objectionable color to the material. Accordingly, the production of a pure white product, suitable for use as a pigment, for example in the coating composition applied to coated papers, is rather expensive and, therefore, it is usable only in the coating of relatively high-grade papers.

It has been a primary object of the present invention to simplify the procedure employed in the production of satin white and to lessen the expense involved so that this product may be used more extensively in the coating of papers, including those of cheaper grades. Toward this end the improved method makes it possible to employ ordinary alum from which the usual iron content has not been removed.

Another object of the invention has been to produce an improved product which is primarily satin white, or calcium sulfo-aluminate, but which contains a small amount, not exceeding about 10%, of calcium sulfite. It has been found that the presence of the calcium sulfite in no way detracts from the brightness, gloss and opacity-producing power of the material but rather enhances these properties and at the same time presents other distinct advantages. For example, the mixture or combination of satin white and calcium sulfite has been found to flow much more freely than satin white alone. This facilitates the application of a coating embodying satin white to the surface of paper to be coated. Moreover, it has been found that a mixture of, say 1 to 10% calcium sulfite and 90 to 99% satin white, on an air dry basis, may be used in the coating of paper with a smaller amount of casein or other adhesive substance than is required by ordinary satin white alone. Pure satin white requires a relatively large amount of casein to bind it firmly to the fibers of the sheet, but for some reason, the presence of a comparatively small amount of calcium sulfite greatly reduces the casein requirement.

In the production of the improved satin white, which, as indicated above, is in reality a mixture or combination of satin white and calcium sulfite, the two constituents are precipitated simultaneously. This not only brings about a desirable, intimate intermixture of the two ingredients in the desired proportion but it accomplishes this result at a minimum of expense and enables the use of a relatively low grade of alum which has not been treated to remove its iron content. Moreover, there may be some chemical combination between the constituents due to coprecipitation, since the mixture of the two ingredients separately formed does not have the same improved characteristics.

In the conduct of the improved process a solution of unpurified alum is subjected to the action of gaseous SO_2 until it becomes saturated with SO_2. The alum solution used for this purpose could be a saturated solution, in which case it would contain approximately one pound of alum for each pound of water. This would be particularly satisfactory if such a solution would also dissolve the full amount of SO_2 normally soluble in the water present, i. e., about 10% by weight. However, it has been found that when the water is saturated with alum, it will dissolve much less SO_2 than is soluble in plain water. Ordinarily, therefore, it is desirable to introduce more SO_2 than will dissolve in a saturated solution of alum, in order to increase the calcium sulfite content of the resulting mixture. For this purpose it is preferable to employ an alum solution containing between 30 and 45%, by weight, of alum.

In a typical operation, in accordance with the invention, an alum solution consisting of 45% alum by weight and 55% water was saturated with sulfur dioxide. It was found that a liter of the alum solution weighing 1310 grams would

dissolve about 30 grams of sulfur dioxide. In theory, the 720 grams of water, present in this amount of solution, should have dissolved about 72 grams of sulfur dioxide, i. e., about 10% of the weight of the water, at room temperature. However, the presence of the alum, with its common ion effect, served to reduce the solubility of sulfur dioxide. This solution of alum and SO_2 was then added to milk of lime containing sufficient lime to provide a ratio between CaO and SO_3 of 1.67. This quantity of lime is in excess, by about 10%, of that required to react fully with the alum and SO_2 to produce satin white, of the formula hereinabove given, and calcium sulfite. The resulting mixture, therefore, must have contained a small amount of free lime, or else the satin white produced was not of the composition indicated by the formula. A sample of the mixture was analyzed and found to contain 3.56% calcium sulfite on the air-dry basis. This mixture, when utilized in a coating composition, was found to possess greater brightness and gloss-producing powers than straight satin white produced from the same lime and alum without the addition of SO_2. It was also found to have certain other advantages from the standpoint of such use. Its viscosity in a water suspension containing a predetermined amount of water in relation to the weight of the solids was lower, i. e., its fluidity was greater, than for a corresponding suspension of the straight satin white. Moreover, its casein requirement was less than for the straight satin white. Thus, in producing a coating composition sufficiently sized to be good to a No. 5A graded Dennison wax, a substantially smaller amount of casein was required for the improved mixture than for the straight satin white. For example, a typical sample of the latter required 30% of casein, based upon the air-dry weight of the satin white, to make it safe to a No. 5A wax while the improved mixture required only 27% of casein, for the same purpose, the coatings being of equal weight, about 18 lbs. per ream. The increased fluidity of the improved mixture not only simplifies the intermixture of the lime and alum and reduces the amount of water required to be used with it in the production of a coating composition, and hence reduces the amount of water which must be eliminated in the driers, in the process of forming coated papers, but it also appears to hasten the reaction between the lime and the alum and SO_2. This reaction is completed in a relatively short time so that the mixture may be used promptly after it has been formed. The usual seasoning or aging period required in the production of satin white may be eliminated. Moreover, the increased fluidity of the improved product renders it more suitable for use as a coating pigment in machine coating operations. Thus, this product may be used to advantage in the machine coating of ground wood papers and when so used the age deterrent property of calcium sulfite will serve to prolong the life of the paper.

In another typical operation, in accordance with the invention, a solution of alum, consisting of 30% alum and 70% water by weight, was first formed and this solution was then saturated with SO_2. It was found capable of dissolving 50 grams of sulfur dioxide per liter of solution. This solution of alum and SO_2 was then added to milk of lime containing such an amount of lime as to provide a ratio of CaO to SO_3 of 1.75. Upon analysis of the resulting mixture, it was found to contain 9.7% calcium sulfite, by weight, on an air-dry basis. This mixture was also found to have excellent properties for coating pigment purposes, superior to those of straight satin white produced from the same raw materials. Its viscosity was considerably lower, its brightness higher, and its gloss substantially the same. The casein requirement of the improved mixture was about 27% as compared with 30% for the straight satin white, in providing compositions safe to a No. 5A Dennison graded wax when applied in coatings of the same weight.

As a result of various operations under different conditions, it has been found that a substantial improvement over ordinary satin white is produced by mixtures containing anywhere between 1 and 10% calcium sulfite with the balance substantially all satin white. It has been desirable, moreover, as a result of these operations, to maintain the CaO to SO_3 ratio above mentioned between about 1.6 and 2.00. Preferably, it should be maintained between 1.75 and 1.8. Within this narrower range the greatest improvement in fluidity or viscosity is found. In all instances the viscosity of the mixture was found to be lower than for straight satin white but when combined with casein, the viscosity of the mixture was in some instances found higher than for straight satin white with casein. If the indicated ratio is carried below 1.6 or above 2.00, the viscosity of the mixture with casein seems to be unpredictable and at times it is unsatisfactory. There is some advantage, also, from the standpoint of gloss and brightness in having the ratio within the narrower limits specified. The casein requirement of the improved mixture has been found in some instances to be reduced as much as 20%, or even 30%, below that of straight satin white.

While it is ordinarily preferred to first dissolve the alum in the water, thereby enabling the use of hot water which may then be cooled before introducing the SO_2, these operations may, if desired, be reversed. The desired amount of SO_2 may first be introduced and the alum subsequently dissolved.

In lieu of introducing gaseous SO_2 into the alum solution, moreover, other means may be employed for introducing the sulfite ion into the solution. For example, a strong solution of sulfurous acid or of calcium bisulfite may be separately formed and added to a saturated alum solution.

In the practice of the present invention, the iron in the alum, which would ordinarily discolor the satin white produced in the reaction between the alum and the milk of lime, is apparently converted into some form in which it produces no discoloration in the improved mixture. This product is as white as if iron-free alum had been used. Possibly this is due to the reducing action of the SO_2 which may convert the ferric ions to ferrous ions whose salts produce little or no discoloration of the final product.

It is preferred to incorporate between 3 and 10% of calcium sulfite in the mixture, but greater or smaller amounts may be employed, if desired, with good results. For example, as little as 1% of the mixture may be calcium sulfite with good results, particularly if the CaO to SO_3 ratio is relatively high, say around 1.8. Larger amounts, in excess of 10%, of calcium sulfite are also advantageous but it is difficult and more expensive to co-precipitate a greater percentage with the satin white. If a relatively small amount is de-

sired, a correspondingly small amount of SO_2 is employed so that the alum solution used in the process is not saturated with SO_2. If a relatively large percentage of calcium sulfite is desired, a greater amount of water is employed, i. e., it is less completely saturated with alum and this greater quantity of water is then fully saturated with SO_2. The alum solution may, for example, consist of only 20% alum in 80% water. The same result may be accomplished by maintaining a higher percentage of SO_2 in solution in a saturated or more concentrated alum solution through the use of pressure.

Preferably, the milk of lime employed in the process is at a concentration, around 150 g./l., at which it may be readily pumped, stirred and screened. Good results may, however, be obtained by the use of milk of lime at higher or lower concentrations (say between 100 and 200 grams per liter) so long as too great a burden is not placed upon the mixing equipment and the conditions are such that a relatively fine precipitate of calcium sulfite is formed.

By maintenance of the proper ratio of CaO to SO_3, the pH of the resulting mixture may be kept well on the alkaline side. It should have a pH above 10 and preferably in the neighborhood of 11.6 or even 11.8.

While the invention has been described in considerable detail in the foregoing, it will be understood that various changes may be made in the method and in the resulting product without departing from the general principles and scope of the invention. The terms and expressions employed herein have been used as terms of description and not of limitation.

What I claim is:

1. A method of producing a pigment substance which comprises dissolving alum in water, dissolving sulfur dioxide in the resulting alum solution, and adding the solution of alum and sulfur dioxide to a milk of lime suspension.

2. A method of producing a pigment substance which comprises dissolving alum and sulfur dioxide in water and adding the resulting solution to a milk of lime suspension.

3. A method of producing a pigment substance which comprises forming a substantially saturated solution of alum and sulfur dioxide in water and adding the same to a suspnsion of lime to co-precipitate satin white and calcium sulfite.

4. A method of producing a pigment substance which comprises forming a substantially saturated solution of alum, introducing gaseous sulfur dioxide into said solution until it is substantially saturated with said sulfur dioxide, and then adding said solution to a milk of lime suspension.

5. A method of producing a pigment substance which comprises forming a non-saturated solution of alum, substantially saturating said solution with SO_2, and then adding said solution to a milk of lime suspension.

6. A method of producing a pigment substance which comprises forming a substantially saturated solution of alum with sulfur dioxide in solution therein, and adding said solution to a milk of lime suspension.

7. A method of producing a pigment substance which comprises forming a solution of alum containing between 20 and 50% alum by weight, dissolving sulfur dioxide in said solution, and then adding said solution to a milk of lime suspension.

8. A method of producing a pigment substance which comprises forming a solution of alum containing between 20 and 50% alum by weight, dissolving sulfur dioxide in said solution, and then adding said solution to a milk of lime suspension, the ratio of the CaO to the SO_3 present in said suspension upon the addition of said solution thereto being between 1.6 and 2.00.

9. A method of producing a pigment substance which comprises co-precipitating satin white and calcium sulfite by reacting a milk of lime suspension with a solution of alum and sulfur dioxide.

10. A method of producing a pigment substance which comprises co-precipitating satin white and calcium sulfite by reacting a milk of lime suspension with a solution of alum and sulfur dioxide, the ratio of CaO to SO_3 in said reaction being between 1.6 and 2.00.

11. As a coating pigment a co-precipitated intermixture of satin white and calcium sulfite in a finely divided state.

12. As a coating pigment a finely divided, co-precipitated mixture of satin white with iron impurities in a ferrous state and calcium sulfite.

13. As a coating pigment a finely divided, co-precipitated mixture of satin white with iron impurities in a ferrous state and calcium sulfite, the calcium sulfite comprising between 1 and 10% of the mixture on an air-dry basis.

14. As a coating pigment a finely divided, co-precipitated mixture of satin white and calcium sulfite, the calcium sulfite being between 1 and 10% of the mixture, and said mixture having a ratio of CaO to SO_3 of between 1.6 and 2.00.

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