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WATER-REPELLENT ULTRAMARINE

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This invention relates to a water repellent ultramarine.

There is a considerable demand for a water repellent ultramarine particularly for such purposes as the blueing of coal for trade-marking purposes. Ordinarily an ultramarine when applied to coal or other surfaces can be caused to gather principally in the cracks of the solid substrate from a water suspension. However, the coloring thus produced is not permanent because it washes off when the coal is exposed to the weather and particularly to the rain, and similar problems are presented with other applications of ultramarine from water suspensions to insoluble substrates.

It has been tried in the past to incorporate ultramarine with rosin size and then to precipitate an insoluble resinate such as an aluminum resinate. This product has been applied to the blueing of coal and similar problems but without great success; adhesion is insufficient and the product still washes off. This problem therefore may be considered as one of combined adhesion and water repellency.

The difficulties encountered with the resinate suspensions which have been used before may be due to a number of factors. Without intending to limit the present invention to any particular theory of action, I believe that at least one factor is the characteristic of the film or coating of insoluble resinate which is produced, and it is my belief that this film is not sufficiently sticky and oleaginous so as to cause good adherence. Probably another factor is that the film itself does not show a sufficient affinity for the surface of the coal to produce good adhesion. Probably there are other factors also involved.

According to the present invention ultramarine is coated with a film of insoluble fatty acid compounds. These compounds may be either water insoluble soaps such as soaps of aluminum, magnesium, calcium, tin, or zinc, or in some cases the free fatty acids themselves. The higher fatty acids which are used in the present invention and which form insoluble compounds are in general useful, but I find that the best results are obtained with oleic acid or coconut oil acids and similar lower molecular acids. While therefore useful products may be produced with the other fatty acids, I prefer to use compounds of oleic acid.

Since the purpose of this invention is to produce a suspension of ultramarine coated and associated with the insoluble higher fatty acid compounds, any suitable method of producing this

coating may be used. Thus, for example, a suspension of ultramarine in a solution of a soluble higher fatty acid compound such as soluble alkali metal soaps may be prepared and then the insoluble compound precipitated, for example by adding a salt of a metal which forms an insoluble soap, or in some cases an acid which will form the insoluble free acid. In the case of very dilute suspensions such as are used, for example in the blueing of anthracite coal, the amount of calcium and magnesium salts in hard water may in some cases be sufficient to produce the desired insoluble fatty acid compound.

Since the ultramarine produced by the present invention is highly water repellent and for that reason not readily dispersible in water, it is frequently desirable to incorporate in the suspension of the pigment in water, a soluble wetting or dispersing agent so as to facilitate thorough dispersion and ready adherence. I have found that the most satisfactory dispersing agents are of the diethyleneglycol mono-ether type. The monobutyl ether of diethyleneglycol is particularly useful. The dispersing agent may be incorporated into the suspension at any stage of its manufacture. Best results are, however, obtained when the wetting agent is incorporated with the soluble soap solution before precipitation of the insoluble fatty acid compound onto the ultramarine. The finest and most uniform coating and best adherence appears to be produced when the dispersing agent is introduced at this stage, and this constitutes the preferred method of introduction, although the invention is not limited thereto.

Since the most important large commercial use for the water repellent ultramarine of the present invention is in the blueing of anthracite coal for trade-mark purposes, the invention will be described in greater detail in conjunction with the production of suspensions of water repellent ultramarine suitable for application to the coal. The effectiveness of the coating and its water repellency are tested by coating anthracite coal in the standard manner and then subjecting it to washing for an hour under a shower of water.

While the product of the present invention is used on a large scale in the blueing of coal, and this is its most important commercial use at the present time, the process of blueing coal and the product obtained are not claimed in this case, but form the subject matter of my copending application Serial No. 426,289, filed January 10, 1942.

The invention will be described in detail in con-

nection with the following specific example, the parts being by weight.

Example 1

14 oz. of caustic soda are added to 8 lbs. of cold water and 1.6 lbs. of mono-butyl ether of diethyleneglycol are added. The solution is heated to 50-60° C. by blowing in steam and then 6 lbs. of oleic acid are added. The mixture is agitated and heated to the boil and held there with continued agitation until the solution is quite clear and a sample dissolves in water completely leaving no oil film. This requires about one hour. After the clear solution is obtained, 2.4 lbs. of mono-butyl ether of diethyleneglycol are added and heating is continued for about fifteen minutes. The amount of water present at this time including the condensed steam should be about 10 lbs. The solution is then cooled to 40-60° C. 1,000 lbs. of ultramarine, preferably very finely ground, are put in a vessel such as a dough mixer. The mixing mechanism is started and while the ultramarine is turned over, sodium oleate solution is slowly and very uniformly added to it. After all of the oleate has been added, the material is finally passed through a hammer mill in order to obtain a very complete distribution of the solution over the ultramarine.

The water repellent ultramarine produced can be used in blueing coal by dispersing it in water to form a homogeneous slurry, for example, 100 lbs. of ultramarine may be dispersed in about 10,000 lbs. of water. To this dispersion there is then added an amount of aluminum sulfate considerably in excess of that theoretically necessary to react with the sodium oleate to form aluminum oleate and sodium sulfate. Satisfactory results are obtained with about 4 lbs. of aluminum sulfate per 100 lbs. of ultramarine. The suspension can then be sprayed onto coal in the usual manner, and after drying forms an adherent deposit mainly in the depressions of the coal which is not washed off to any appreciable extent when the coal is immersed in water or exposed to a shower of water. The ultramarine particles are coated with a water repellent aluminum oleate which has good adherence and which after drying does not redisperse in water. The coating is absent or light on the flat surfaces of the coal, and concentrated in the depressions.

Example 2

The procedure of Example 1 is followed except that instead of 4 lbs. of aluminum sulfate an equivalent amount of magnesium sulfate is added. The product obtained is very similar in its properties to that in Example 1.

Example 3

The procedure of Example 1 is followed except that an equivalent amount of calcium chloride is substituted for the aluminum sulfate. A product is produced which adheres to coal even better than the product of Example 1.

Example 4

In the procedure of Example 1 an equivalent amount of stannic chloride is substituted for the alum. The product obtained shows an adherence to coal substantially the same as that possessed by the calcium product of Example 3.

Example 5

An equivalent amount of zinc chloride is substituted for the aluminum sulfate of Example 1

and a product similar to that of Example 3 is obtained.

Example 6

Instead of using aluminum sulfate in the procedure of Example 1, sufficient sulfuric acid is used to neutralize all of the alkali present and to precipitate free oleic acid. The product obtained has excellent adherence to coal and resembles the products of Examples 3, 4, and 5.

Example 7

The procedure of Example 1 is followed using a very hard water but no alum is introduced. A product is obtained which is similar to that of Examples 2 and 3 depending on the hardness of the water used.

The properties of the products of the seven examples are shown in the following table which gives the shade before washing for an hour under a shower of fresh water, after washing, and the visibility in both the wet state and under artificial light. Example 1 is the product which is at present used on a large scale in the blueing of anthracite coal and will be referred to as the type, other shades being compared to it.

Example	Before washing shade	After washing	Visibility wet	Visibility artificial light
1	Type	Type	Type	Type
2	Similar to type	Similar to type	Similar to type	Similar to type
3	do	Better than type	Better than type	Do.
4	do	do	do	Do.
5	do	do	do	Do.
6	do	do	do	Do.

The extraordinary difference between the products of the present invention and that obtainable in the past using resins presents a complex problem because the individual ultramarine particles when examined under the microscope do not permit accurate determination of the differences, as the film is translucent or transparent and is hence not readily visible. The result of the present invention is all the more surprising because ordinary water repellent pigments including prior water repellent ultramarine cannot be dispersed in water. They clump together to form non-homogeneous suspensions and therefore cannot be used in the form of water suspensions. The dispersing agent such as the ether of diethyleneglycol is needed to impart a temporary dispersibility to the coated ultramarine. However, if this dispersibility were permanent, the product would wash right off. Such, however, is not the case of the examples in the table above. This temporary dispersibility which disappears on coating the coal may be due to a number of factors and it is not desired to limit the present invention to any particular theory. I believe, however, that at least one factor and perhaps the most important factor is due to a removal of the dispersing agent in solution in the water in which the ultramarine is suspended and quite probably also by evaporation as the coating dries. Possibly other factors are involved as chemical changes may take place during the drying of the coating. I believe, however, that the permanent water repellency of the dried coating is primarily due to physical removal of the dispersing agent and this is advanced as the most probable explanation of the surprising change which takes place in the nature of the ultramarine when its suspension is applied to a surface and dried.

In the examples, oleic acid has been described as the higher fatty acid. The acids of cocoanut oil give equally good results. Pure acid is not necessary, technical grades being useful, and similar results are obtained with other acids such as palmitic and stearic although the film in the case of oleic and cocoanut acids shows somewhat better adherence. Other alkyl ethers of diethyleneglycol may be used as dispersing agents such as the mono-ethyl ether and other water-soluble dispersing agents may be used such as for example alkali metal salts of higher alkyl sulfuric acids, salts of alkyl naphthalene sulfonic acids, salts of esters of sulfosuccinic acid, and the like. Best results are however obtained with the mono-alkyl ethers of diethyleneglycol which are therefore the preferred dispersing agents.

What I claim is:

1. A method of producing a water dispersion of ultramarine capable of drying on a surface to a water-repellent non-dispersible ultramarine coating which comprises homogeneously coating finely ground ultramarine with a very thin film of a soluble soap by admixing a solution of said soap with the ultramarine until homogeneous coating results and suspending the coated ultramarine in water in the presence of a water soluble volatile dispersing agent and in the presence of a salt of a polyvalent metal capable of reacting with the soap coating the ultramarine to transform the former into the salt of the polyvalent metal and the fatty acid of the soap.
2. A method of producing a water dispersion of ultramarine capable of drying on a surface to a water-repellent non-dispersible ultramarine coating which comprises homogeneously coating finely ground ultramarine by admixing therewith a small amount of a water solution of a soluble soap and a water soluble volatile wetting agent while kneading the ultramarine, continuing the kneading until a homogeneous coating of the ultramarine is effected, and suspending the coated ultramarine in water containing the salt of a polyvalent metal capable of reacting with a soap coating to transform the latter into a soap of the polyvalent metal.
3. A method of producing a water dispersion of ultramarine capable of drying on a surface to a water-repellent non-dispersible ultramarine coating which comprises homogeneously coating finely ground ultramarine with a very thin film of an alkali metal oleate by admixing a solution of said oleate with the ultramarine until homogeneous coating results and suspending the coated ultramarine in water in the presence of a water soluble volatile dispersing agent and in the presence of a salt of a polyvalent metal capable of reacting with the alkali metal oleate coating the ultramarine to transform the former into the salt of the polyvalent metal and oleic acid.
4. A method of producing a water dispersion

of ultramarine capable of drying on a surface to a water-repellent non-dispersible ultramarine coating which comprises homogeneously coating finely ground ultramarine by admixing therewith a small amount of a water solution of an alkali metal oleate and a water soluble volatile wetting agent while kneading the ultramarine, continuing the kneading until a homogeneous coating of the ultramarine is effected, and suspending the coated ultramarine in water containing the salt of a polyvalent metal capable of reacting with the oleate coating to transform the latter into an oleate of the polyvalent metal.

5. A method according to claim 1 in which the material added to produce an insoluble fatty acid compound is an aluminum salt.

6. A method according to claim 3 in which the material added to produce an insoluble fatty acid compound is an aluminum salt.

7. A method according to claim 4 in which the material added to produce an insoluble fatty acid compound is an aluminum salt.

8. A method according to claim 1 in which the material added to produce an insoluble fatty acid compound is a calcium compound.

9. A method according to claim 3 in which the material added to produce an insoluble fatty acid compound is a calcium compound.

10. A method according to claim 4 in which the material added to produce an insoluble fatty acid compound is a calcium compound.

11. An aqueous suspension of ultramarine coated with a thin film of a water insoluble salt of higher fatty acid and a polyvalent metal associated with a water soluble volatile wetting agent, said dispersion being capable of drying to produce a coating of water-repellent ultramarine which is not redispersible in water.

12. An aqueous suspension of ultramarine coated with a thin film of aluminum oleate associated with a water soluble volatile wetting agent, said dispersion being capable of drying to produce a coating of water-repellent ultramarine which is not redispersible in water.

13. An aqueous suspension of ultramarine coated with a thin film of calcium oleate associated with a water-soluble volatile wetting agent, said dispersion being capable of drying to produce a coating of water-repellent ultramarine which is redispersible in water.

14. A product according to claim 11 in which the wetting agent is a mono-alkyl ether of diethylene glycol.

15. A product according to claim 11 in which the wetting agent is mono-butyl ether of diethylene glycol.

16. A dispersion according to claim 12 in which the dispersing agent is mono-butyl ether of diethylene glycol.

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