

UNITED STATES PATENT OFFICE

2,568,599

FLATTING AGENTS

William A. Weidlich, North Plainfield, and James E. Davis, Bound Brook, N. J., assignors to Interchemical Corporation, New York, N. Y., a corporation of Ohio

No Drawing. Application February 5, 1947,
Serial No. 726,740

3 Claims. (Cl. 106—175)

1

This invention relates to new flatting agents particularly useful in the matte coating compositions of the lacquer and synthetic resin type, characterized by usual flatting power combined with film toughness and particularly with marked resistance to yellowing.

While many protective and decorative finishes are glossy, it is often desired to obtain finishes which are more or less matte and free from specular reflection, either for the decorative effect (as in furniture finishes) or for the utilitarian effect (as in finishes for photographic devices, where a non-reflecting surface is essential). Such an effect can be obtained by the use of very high percentages of pigment (e. g., flat wall paints, automobile undercoaters); but it is often desirable to get the same effect without loading the film with pigment either because the film properties of a lightly pigmented finish are desired, or because a transparent finish is desired.

To obtain this effect, the coating composition may be designed with an unbalance between the various film-forming ingredients and solvents, so that, on drying, a portion of the film is precipitated while the rest of the materials are still in solution. A very satisfactory flatting effect may be obtained in this fashion, and by careful compounding with certain classes of ingredients, exceedingly tough, transparent dull films are often obtainable. However, the method is not applicable to those classes of film-forming materials which cannot be precipitated and retain toughness of film. Furthermore, even with the best flat finishes of this type, the degree of flatness varies with the drying conditions, and uniform results cannot be obtained unless drying conditions are maintained absolutely uniform. Because of the difficulties involved in maintaining absolutely uniform drying conditions, this type of flat composition is used only in isolated instances.

The trade in general has adopted the use of powders which are relatively insoluble in the coating compositions, and which can be dispersed therein to yield films which are translucent because of the similarity in refractive index between the flatting agents and the film-forming solids, and are flat because of the fact that the insoluble flatting agents break up the light hitting the surface of the film. The flatting agents generally employed fall into two classes—inorganic transparent inerts, and organic flatting agents.

The common inorganic inerts are siliceous materials, such as infusorial earth, silica, silica gel, some talcs, etc. They are essentially pigments,

2

capable of staying on the surface of coatings while wet and during film formation, and which are transparent because their refractive indices approach those of the vehicles, and are able to produce effective flatting because of the uneven surface and uneven light reflection so formed. They have three principal disadvantages. First, they are never perfectly transparent when a film of very low reflectivity is wanted. Second, they settle very badly to hard dry cakes upon storage which stir in with difficulty. This appears to be a property associated with their particle size and shape. Finally, the films produced are essentially pigmented films, so that where high flexibility is desired, as in artificial leather, the films are unsatisfactory because they craze on flexing.

The common organic flatting agents comprise certain transparent uncolored heavy metal soaps (magnesium, the alkali earths, zinc and aluminum soaps of fatty acids), and the waxes. These materials generally produce more transparent films than the inorganic flatting agents, since they are more nearly similar in refractive index to the film-forming agents. Furthermore, because of their low specific gravity, and because of their similarity in general constitution to the vehicles, they stay in suspension better, settling into flocculates which are easily stirred back into uniform dispersion. Because of these advantages, they are preferred for transparent interior finishes and the like. They have, however, certain marked disadvantages. While they do not break up a film as badly as the inerts, the films containing these agents also show crazing when flexed, as on artificial leather, except in the case of the most soluble soaps, which are extremely difficult to handle. Certain of the soaps hydrolyze when the films are exposed to water, causing an objectionable whitening of the film. Finally, the waxes and soaps are all more or less soluble in hydrocarbon solvents, particularly at elevated temperatures, thereby suffering loss of flatness. Also improper milling, resulting in high temperature, will cause loss of flatting power. These flat materials cannot be used in finishes designed to be dried at elevated temperatures. The metallic soaps of fatty acids are sensitive to humidity and may cause great delay in drying of the films, as well in varnishes as in lacquers. The films formed in high humidity have a cheesy appearance.

The known flatting agents cause much less trouble in oleoresinous varnishes, where the solvents are present in relatively small proportion, and are largely aliphatic hydrocarbons in char-

3

acter, than in lacquers and synthetic resin compositions, where larger proportions of more powerful solvents are used.

There has recently been developed a new type of flattening agent which has reasonably good resistance to solution in the solvents of lacquer and synthetic resin vehicles, while yielding tough films. These pigments are soaps of hardened rosin (e. g., maleic treated rosin, phenol resin modified rosin, and the like), preferably coated with an originally water-soluble lacquer-insoluble vehicle such as methyl cellulose. These are described in the Auer U. S. Patent No. 2,363,489. However, these flattening agents show a definite tendency to yellow when exposed to light.

We have discovered how to prepare a tough non-crazing solvent-resistant flattening agent. Our method involves the use of an adduct of an alpha beta unsaturated acid and a terpene, from which is prepared the aluminum soap in pigment particle size. Preferably this is coated with an originally water-soluble lacquer-insoluble vehicle such as methyl cellulose or egg albumin. These substances, while acting to some extent as a binder for the pigment, also act to prevent solution of the pigment in organic solvents. Instead of the aluminum soap we may use other insoluble soaps such as barium, magnesium and in general the alkaline earth metal soaps.

The adduct of alpha beta unsaturated acid and terpene (commercially available as Petrex acids, the composition and manufacture of which are disclosed in U. S. Patents 1,832,298; 1,978,598; 1,993,025-037; 2,011,707; 2,022,149; 2,025,947; and 2,047,004) is first converted to a soluble salt by reaction with alkali and then the insoluble soap is precipitated by reaction of a solution of the soluble salt of the terpene adduct with a solution of a salt of such metals as magnesium, aluminum, zinc or the alkaline earth metals, in the presence or absence of methyl cellulose, egg albumin or the like. We can use either the esters or the unesterified products of these terpene-acid adducts. If desired, the flat may be precipitated on a mineral extender such as silica.

We can use either the esters or the unesterified products of the terpene-acid adducts, but prefer the esters. It is desirable that the adduct have an acid value considerably above 40 although the reaction will take place with adducts having acid values as low as 40-50. The essential property of these adducts is that they will react in the presence of alkali to give soluble salts of the adducts. Alkalies that have been used successfully include sodium hydroxide, borax and amines. Examples of our invention are:

EXAMPLE I

Solution 1.—Weigh 150.0 grams of Petrex SS Resin Solution (Hercules Powder Co.—a special alkyd made from terpene-maleic anhydride adduct, 70% solution in alcohol) into a beaker with about 2000 grams of water. Add 45 grams of sodium hydroxide and raise the temperature with continual stirring until dissolved.

Solution 2.—While solution #1 is cooling, add 15 grams of methyl cellulose into a little hot water, and break up. Add enough cold water to equal 1600 grams of water, and stir until dissolved. Methyl cellulose is soluble in water below 140° F. to 160° F., but is precipitated by water above 140° F. to 160° F. Cool solution #1 to below 135° F., and strain solution #2 into #1.

Solution 3.—Dissolve 130 grams of iron-free aluminum sulfate into 500 grams of cold water,

4

and add it slowly with stirring into the mixture of solutions #1 and #2. The pH of the precipitation should come to about 7.0 before all the aluminum sulfate is added. Test for complete precipitation by filtering 2 cc. and 1 drop of hydrochloric acid (39%). If no resin is precipitated, add 3 cc. of hydrochloric acid to pH 5.5 or 6.0 for easy filtering. Heat to boiling point, and hold for 10 to 30 minutes, and filter hot. Remove soluble sulfates by washing with water above 160° F. Test for completeness of wash by adding 5 drops of 5% barium chloride solution to 10 cc. of wash water.

EXAMPLE II

Solution 1.—Weigh 300 grams of Petrex A7HT (Hercules Powder Co.—75% solution of a diglycol ester of a terpene-maleic acid adduct in alcohol) into a beaker with about 2000 grams of water. Add 110 grams of mono-ethylamine and raise the temperature with continual stirring until dissolved.

Solution 2.—Dissolve 175 grams of iron-free aluminum sulfate in 500 grams of cold water, and add it slowly with stirring into solution #1. Test for complete precipitation by filtering 2 cc. of the solution and adding 1 drop of hydrochloric acid (39%). If the resin is precipitated, add sufficient hydrochloric acid to the mixture to ensure easy filtering, about 3 cc. will generally be sufficient. Heat to boiling and hold for 10 to 30 minutes, and filter hot. Wash the residue with water until free of soluble sulfates as indicated by testing the filtrate with barium chloride solution. After drying, this flat pigment is ready for use in making flat lacquer pastes.

EXAMPLE III

Solution 1.—Weigh 267 grams of Petrex A-5 (Hercules Powder Co.—75% solution of an ethylene glycol ester of terpene-maleic acid adduct in alcohol) into a beaker with about 200 grams of water. Add 40 grams of sodium hydroxide and raise the temperature with continual stirring until dissolved.

Solution 2.—Dissolve 175 grams of aluminum sulfate in 500 grams of cold water, and add it slowly with stirring to solution #1. Test for complete precipitation of the aluminum soap by filtering 2 cc. of the mixture and adding 1 drop of hydrochloric acid (39%). If no resin is precipitated, add 3 cc. of hydrochloric acid and after heating the mixture to boiling for 10 to 30 minutes, filter hot. Remove soluble sulfates by washing with water. After drying the residue, it is ready for use in the preparation of flat lacquer pastes.

A typical flat lacquer paste is made from:

225.0 grams flat pigment of Example 1.
35.5 grams 5-6 Sec. RS type nitrocellulose (alcohol wet).
570.0 grams alcohol.
619.0 grams ethyl acetate.

by grinding in a ball mill for 48 hours.

The incorporation of the flattening agent into various vehicles may be carried out in any conventional manner as by pebble mill, roller mill or the like.

In addition to having reasonably good resistance to solution in the solvents of lacquer and synthetic resin vehicles, the novel flattening agents made in accordance with our invention show some improvement in resistance to light and heat over the heretofore known flattening agents. Films from

5

compositions containing our flatting agent do not show as marked a tendency to turn yellow when exposed to light or heat as do the films formed from compositions containing the flatting agents prepared according to the heretofore mentioned Auer U. S. Patent No. 2,363,489.

The above examples are illustrations of the different embodiments of the present invention and should not be considered as limiting its scope.

We claim:

1. A coating composition which dries to a substantially transparent dull or matte surface, which comprises a normally glossy drying non-aqueous organic film forming vehicle containing hydrocarbon solvents, the films of which are dulled by the incorporation therein of pigment size particles of a soap of a metal of the class consisting of aluminum, zinc, magnesium and alkaline earth metal salts of an adduct of an alpha

6

beta unsaturated dibasic acid with a terpene, and coated with a film deposited from an aqueous solution of methyl cellulose.

2. A composition as claimed in claim 1, in which the soap is that of aluminum.

3. A composition as claimed in claim 1, in which the soap is that of calcium.

WILLIAM A. WEIDLICH.
JAMES E. DAVIS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,363,489	Auer -----	Nov. 28, 1944
2,344,831	Ott -----	Mar. 21, 1944
2,418,450	Auer -----	Apr. 8, 1947