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FLATTING AGENT AND USES THEREFOR

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This invention relates to flat liquid coating compositions and more particularly it has reference to an adjuvant for varnishes, lacquers, and the like which will dull the appearance of the coating prepared therefrom, and methods of utilizing the same.

Until fairly recent times, the most highly regarded finish for wood in connection with which a transparent coating is desired was that prepared by application of a layer of a drying oil varnish over a stained, filled, and shellacked surface and subsequently rubbing down the film of varnish by hand. This gives a dull glossy finish that is still prized, but involves considerable labor by a skilled artisan. The time and labor required makes this process of limited use, and those interested early began seeking for some way of dulling the objectionably bright and harshly reflective surface that is the natural result of drying varnish.

The first major advance was development of the so-called "flat" varnish containing a component which imparted a dull sheen to the final coating without rubbing. In general the adjuvants that impart flatness to the varnish are substances probably having an index of refraction approximating that of the varnish film. The transparency of the varnish is not appreciably affected by satisfactory flatting agents, but the dry surface has a soft glowing luster that is similar to the appearance of varnish which has been "rubbed" with pumice stone and oil by a skilled artisan. Known flattening agents include abestine, clay magnesia, magnesium carbonate, wax, and heavy metal soaps such as aluminum stearate and zinc tungate. Such substances are generally quite useful in drying oil varnishes, but considerable care must be used in making up the varnish. The flatting agent and varnish are usually ground together for rather long periods on a paint mill, often requiring eight hours or more for the grinding operation.

With the introduction of nitrocellulose lacquers, the flatting problem was again raised, but upon finding that the substances which cause varnishes to be flat have a like effect on lacquers, it was believed that flatting of lacquers was relatively simple. To the dismay of lacquer producers, known flatting agents were found to be highly unsatisfactorily for nitrocellulose coating compositions.

The inorganic transparent "pigment" type of flatting agent, necessarily present in small amount, showed a marked tendency to cake and settle in the lacquer vehicle. The resulting agglomerates blurred the film, and inorganic flatting agents were practically eliminated from consideration, leaving wax and insoluble soaps as the only practical flatting agents for lacquer.

It was then found that lacquers flatted with wax were not of practical commercial value. The wax flat is a very clear, hard lacquer, but the wax tends to break up the continuity of the film, making the composition too "short". Over shellac the wax flatted lacquer is actually brittle. This objection, together with the lack of uniformity of raw material, difficulty of grinding, and other manufacturing difficulties has resulted in abandonment of wax as a flatting agent for lacquer. Manufacturers have been forced to use the insoluble metal soaps as the only commercially feasible flatting agent known for nitrocellulose lacquers.

These metallic soaps produce stable suspensions of flatting agent in the lacquer vehicle, and the films of soap flatted lacquer are clear and of a dull luster. For a time, it seemed that the problem of making flat lacquers was solved. The effect of sunlight on such lacquers was not anticipated, and since that effect requires a period of two or three years to develop, the market was well stocked with lacquers containing metallic soaps when serious difficulties in connection with such compositions were presented to the manufacturers.

Soaps tend to break down under the action of ultra-violet light, and the decomposition products are markedly hygroscopic. The soap, which acts as a water-proofing component in the original lacquer, actually absorbs water from the air after decomposition, and the lacquer film becomes fogged. In extreme cases the surface film turns to an opaque white, and the manufacturer is faced with the alternative of suffering a loss of reputation or adjusting a claim of considerable size as compared to his price for the original sale of lacquer.

Immediate steps were taken in the attempt to produce a "waterproof" soap. The soaps of wood oil acids were tested extensively with poor results. Generally, the films obtained with metallic tungates and the like were obscured by a blue haziness that could be overcome only with great difficulty.

Diatomaceous earth is used as a flatting agent for lacquers and varnishes, but I have found that larger quantities are required, very substantially longer grinding is necessary and, whereas with aerogels one obtains a clear film,

diatomaceous earth tends to produce a cloudy or milky film. It has been suggested that a metallic tungate of great purity is superior to previously known substances as a flatting agent for nitrocellulose lacquers. As is well known, tung oil is a material of complex composition, and it follows that purification to any considerable degree is a difficult and expensive process. After formation of the metallic tungate, it has been found necessary to carry the flatting compound through intricate purification steps in order to positively remove metal salts and other impurities as they may cause serious trouble if not eliminated.

It is seen that prior to this invention, the art did not know of a flatting agent capable of general application which could be prepared and incorporated into the finished coating composition with no more than moderate cost.

It has now been discovered that finely divided gels which retain substantially the original structure in the coating composition are excellent flatting agents for various types of coating compositions. Such materials may be incorporated in the liquid coating material by replacement of the swelling agent or original continuous phase, or they may be converted to aerogels and ground into the liquid on a paint mill in the well known manner.

A primary object of this invention is the provision of a flat coating composition.

Another object of the invention is to provide a stable flatting agent of improved characteristics.

The invention further provides the definition of a class of substances which are flatting agents of general application and from which may be chosen a particular adjuvant particularly suitable as a flatting agent for any given liquid coating composition.

In general it may be stated that the original gel structure can be maintained unimpaired if the original continuous phase is displaced without the formation of interfaces in the pores of the gel. The surface tension at such interfaces is now believed to exert sufficient force to collapse the gel to a greater or less extent depending on the nature of the interface and the density of the gel.

One manner in which the flatting agents of the present invention may be incorporated in the coating composition is by replacement of the original continuous phase of a gel with the vehicle of the liquid to be flatted. A liquid existing as the continuous phase of a gel may be practically completely replaced by another liquid if the two are miscible. The gel is immersed in successive baths of the replacing liquid until the replacement has proceeded to a satisfactory extent. By a series of similar replacements it is possible to prepare a gel having any desired liquid as the continuous phase, no matter what the original continuous phase. Thus a hydro-gel may be converted to an ether-gel by first forming a gel in which the continuous phase is alcohol. If the original continuous phase is miscible with the vehicle of the coating composition, preparation of a gel containing the vehicle from the original gel may be accomplished in a single step. The gel as precipitated is immersed in successive baths of the vehicle until the continuous phase is composed of a liquid the major proportion of which is the vehicle of the liquid coating composition. The gel may then be incorporated into the final product by grinding the finely divided gel with the liquid coating composition or by adding to such composition a previously prepared slurry of the gel in a portion of the vehicle or of the unflatted coating material. When it is desired to prepare the final composition by addition of a preformed slurry to a portion of untreated liquid (either vehicle or mixture of vehicle and film forming constituent), the gel is added to the liquid with mechanical agitation. A convenient apparatus for making up the slurry is a motor driven stirrer in a jar. More concentrated preparations are easily formed by ball milling a mixture of gel and liquid.

Proportions of gel to coating composition may vary widely according to the nature of the gel, the composition of the unflatted coating material and the properties desired in the finished product. A silica gel may be used as a flatting agent for clear varnish in amounts preferably ranging from 0.2% to 7.0% of gel based on the weight of the solid phase thereof, and it has been determined that a clear varnish containing about 4% or 5% silica gel is a relatively stable suspension forming hard clear films of the desirably dull luster. The preferred proportions recited above are not limiting, but the advantages of this invention may be realized to some extent over an extremely wide range of compositions. Ten per cent or more of gel may be incorporated into a coating composition to form so-called "crackle" finishes which are flat. The prepared liquid coating composition is very short, and the film formed therefrom cracks on drying to form a surface which is very attractive for certain uses.

From the great number of gels known may be chosen a material which will give the desired results and yet be compatible with the components of the liquid coating composition under consideration. Gels of metal oxides and hydroxides as silica, magnesia, thoria, ferric hydroxides, and alumina; and organic gels such as albumin, cellulose, and synthetic resins swollen in suitable solvents are suitable for the purposes of this invention.

An alternative, and in many cases more convenient, method of incorporating my novel flatting agent into the liquid coating composition is to grind into the liquid an aerogel of the type described in United States Patent 2,093,454 to Samuel S. Kistler. When a gel is dried by normal evaporation, the solid structure thereof is collapsed to a large extent. The favored explanation of this phenomenon is that the fine fibers constituting the solid phase of the gel do not possess sufficient mechanical strength to resist the forces exerted by the menisci of the continuous phase as these recede on evaporation. Dried gels which have shrunk on drying are denominated xerogels to distinguish them from the aerogels which are dried without shrinkage of the gel structure.

Aerogels are formed by removal of the continuous phase of a gel under such conditions that the surface tension of the liquid continuous phase is zero or very small. When the continuous phase is a liquid having a very small surface tension at atmospheric temperature, it may usually be removed by drying at ordinary pressure without susbtantial damage to the gel structure. Some petroleum fractions meet this condition, but most liquids which may occur as the original swelling liquid or become the continuous phase by replacement of the original liquid do have appreciable surface tension. The latter type of liquid medium is conveniently removed by heating to above

the critical temperature of the liquid in an autoclave while maintaining the pressure sufficiently high to insure that the continuous phase will remain in the liquid state at all temperatures below the critical. At or slightly above the critical temperature, the liquid in the gel will be converted to gas without attendant formation of menisci and may be allowed to escape without damage to the gel structure.

In handling gels in which the continuous phase is a liquid of inconveniently high critical temperature and pressure, the difficulties of autoclaving at such conditions may be avoided by replacing the continuous phase with another liquid of more suitable properties. Silica aerogel has been prepared from the hydro-gel by replacing water with alcohol in the manner described above and heating the resultant alco-gel to a temperature above the critical temperature of alcohol under a pressure slightly in excess of the critical in an autoclave. The product is a light solid having an apparent specific gravity less than 15% of the actual value and possessing a large proportion of voids in sub-microscopic pores. By variation of the concentration of the original gel and of the conditions of treatment, gels having a percentage of voids ranging from the 30 to 50% normally found in xerogels (silica gels of commerce) to 99% or over may be prepared.

The aerogels have been found to be excellent flatting agents for fluid coating compositions of various kinds. They are ground into the liquid composition with great ease and require a much shorter grinding time than commercial silica gels and similar materials now known to the trade. It is important that the aerogel containing liquid be not ground too long, as prolonged grinding destroys the flatting effect achieved by proper grinding. Further, it has been determined that, as compared to xerogels, the aerogels are effective to the same extent when present in much smaller proportions on the weight of the finished coating composition.

Aerogel containing varnishes, lacquers, and other liquid coating compositions are prepared by making a slurry of aerogel and untreated coating material and grinding the mixture on a paint mill until the aerogel is evenly dispersed throughout the liquid. Alternatively the aerogel may be mixed with a small proportion of the liquid to form a paste or very viscous liquid, and this concentrate is then added to the liquid to be treated.

On the strength of tests conducted, it has been estimated that the aerogels are approximaely 2½ times as effective as xerogels for flatting varnishes and the like. Enormous savings in time and equipment are realized by using aerogels, since it has been discovered that grinding time is reduced tremendously. A clear varnish containing silica xerogel requires about 16 hours grinding, more or less, in order to form a suitable flatted varnish. A proportion of silica aerogel (having an apparent specific gravity of about .10–.15 which will give a varnish comparable to that of the sixteen hour ground xerogel varnish gives a satisfactory varnish after two hours grinding with varnish on the same paint mill. It is believed that the grinding of aerogel must be sufficient to break up agglomerates of gel and disperse them through the mixture but must stop short of the point at which small particles are broken up, since prolonged grinding gives a varnish capable of forming a film which cannot be differentiated from that of untreated varnish on examination with the unaided human eye.

The proportions of gel in the final composition when prepared by grinding in dry aerogel are preferably of the same order as those resulting from the first method described herein. Similarly, dry flatting agents may be the aerogels of any desired substance capable of forming a gel.

It is seen that the present invention includes the preparation of a flat coating composition by incorporating therein a minor proportion of a gel, the solid structure of which is maintained in substantially the form in which it existed at the time the original gel was prepared.

The flatting agents of this invention may serve purposes additional to that of flatting the liquid coating composition. A gel having slight tinctorial value as a chromium oxide gel may be used to give pleasing effects. Also as pointed out above, crackle finishes are obtained from compositions containing an excess of the new flatting agent. The invention also contemplates the use of aerogels of siccatives, such as magnesia aerogel for flatting.

One convenient way of using aerogels according to my invention involves the preparation of a master batch of the vehicle containing the gel, which batch is ground so that little, if any, additional grinding is necessary when the material is added to the varnish or lacquer composition. This enables me to add a flatting agent from the master batch to any finished varnishes or lacquers when, and only when, a flat effect is desired. Furthermore, it is possible to market or distribute a master batch of the flatting agent to be used by the paint and varnish consumer in conjunction with prepared varnishes and lacquers whenever and to the extent the user deems the flat effect desirable. For the purpose of the master batch I grind the aerogel in a varnish or lacquer solvent in sufficient quantities to produce a gel or paste which, however, will disperse readily upon mixing with the lacquer or varnish. For this purpose 8%–12% of aerogel will usually be found sufficient. The mixture may be ground in the usual way until a maximum flatting power is developed, after which it can be stored indefinitely.

I claim:

1. A flat liquid coating composition comprising a film forming liquid and a ground aerogel having in the mixture substantially the structure of the gel as originally formed.

2. A flat liquid coating composition comprising a clear varnish and a ground aerogel having in the mixture substantially the structure of the gel as originally formed.

3. A flat liquid coating composition comprising nitrocellulose, a solvent therefor, and a ground preformed aerogel having in the mixture substantially the structure of the gel as originally formed.

4. A flat liquid coating composition comprising a film forming liquid and a ground silica aerogel having in the mixture substantially the structure of the gel as originally formed.

5. A flat liquid coating composition comprising a clear varnish and a ground silica aerogel having in the mixture substantially the structure of the gel as originally formed.

6. A flat liquid coating composition comprising nitrocellulose, a solvent therefor, and a ground silica aerogel having in the mixture substantially the structure of the gel as originally formed.

7. A flat liquid coating composition comprising

a film forming liquid and a ground alumina aerogel having in the mixture substantially the structure of the gel as originally formed.

8. A flat liquid coating composition comprising a film forming liquid and a ground thoria aerogel having in the mixture substantially the structure of the gel as originally formed.

9. A flatting composition to be added in small amounts to varnishes and lacquers and capable of imparting a flat finish to a film obtained thereby comprising a mixture of an aerogel and a liquid vehicle therefor which is compatible with a varnish or lacquer solvent said gel being ground to impart substantially maximum flatting effect.

10. A flatting composition to be added in small amounts to varnishes and lacquers and capable of imparting a flat finish to a film obtained thereby comprising a mixture of a silica aerogel and a liquid vehicle therefor which is compatible with a varnish or a lacquer solvent, said gel being ground to impart substantially maximum flatting effect.

11. A flatting composition to be added in small amounts to varnishes and lacquers and capable of imparting a flat finish to a film obtained thereby comprising a mixture of an alumina aerogel and a liquid vehicle therefor which is compatible with a varnish or a lacquer solvent, said gel being ground to impart substantially maximum flatting effect.

12. A flatting composition to be added in small amounts to varnishes and lacquers and capable of imparting a flat finish to a film obtained thereby comprising a mixture of a thoria aerogel and a liquid vehicle therefor which is compatible with a varnish or a lacquer solvent, said gel being ground to impart substantially maximum flatting effect.

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