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METALLIZING COMPOSITION

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This invention relates to coating compositions containing metallic powder such as aluminum or bronze powder, commonly called bronzing compositions.

Attempts have been made to produce such coating compositions containing aluminum powder with an oily vehicle such as varnish. They have been marketed in a limited way in the form of suspensions. The suspension is made by mixing the components together in a paint mixer in the manner customary when manufacturing certain paints. Such metallizing composition has not been entirely satisfactory for the reason that the aluminum powder when suspended in varnish or oily vehicle for any period of time tends to darken and lose its luster. It also cakes or settles badly when mixed with thin vehicles, and is difficult to keep in suspension. In addition there are on the market two component metallic powder compositions. The metallic powder as such is packed in one compartment of a two-compartment container. Liquid lacquer or varnish or other oily vehicle is placed in the other compartment. These components are mixed immediately prior to use. In addition, metallic powder mixed with a viscous liquid asphalt or asphalt emulsion to form a paste has been produced. In common with ordinary paints prepared in liquid form, however, such compositions have a considerable bulk due to the vehicle being in liquid form. The cans are costly and occupy approximately the same shelf space as the liquid suspension type paint containers. In addition, compositions so marketed are a fire-hazard on the shelves, usually being stored with or near other goods that will burn.

Bronze and aluminum lacquers are widely known compositions embodying bronze and aluminum powder. They consist of the aluminum or bronze powder accompanied by special solutions of nitro-cellulose and softening agents, etc. The metallic powder is kept separate from the lacquer and mixed at the time of use. After mixing it is important that the mixture be used up quickly without standing. If allowed to stand, some reaction occurs, producing insolubles, which cannot be satisfactorily employed for the purpose intended. Such lacquers are furthermore expensive and their use and availability are correspondingly limited.

The principal object of the present invention accordingly is to produce a metallic powder composition which may be stored and marketed in dry form without the fire-hazard or inconvenience of mixed paint or special volatile or explosive materials, and which may be prepared for application by mixing with a suitable easily procurable inexpensive solvent or vehicle components by the consumer as needed at the point of use without the necessity of mixing machinery. Another object of the invention is to produce a composition which when mixed with solvent and applied will produce a highly flexible coating film, which will be less expensive than the bronzing lacquers and may be allowed to stand after mixing for a considerable period and settle out part of the metal powder without producing any substantial amount of precipitated insolubles such as formed by bronzing lacquers.

We have found in accordance with our invention that a dry base may be prepared and marketed as such, ready to be merely mixed at the time of use with an inexpensive solvent. We have discovered that the liquid after addition of the solvent should be sufficiently thick so that the metal powder does not settle out excessively, and to this end we have present a suitable binder material so that when the volatile constituents of the composition have evaporated this binder will remain behind to form at least a part of the film and preferably also a thickening agent. We have found that the thickener and binder may be constituted by one substance. We may employ two or more substances to secure these results. It is also important that the metallic particles be substantially level and in contact at their edges giving an apparently continuous metallic surface which is bright and shiny. We have found that certain of the binders upon addition of a proper solvent effect this leveling action in themselves. To others a "leveling" agent is preferably added, which serves to produce this condition. It is also important that the resulting paint film be flexible and for this purpose it is desirable that a suitable substance be used.

We have found that an improved composition of this type may be made by mixing with aluminum or bronze powder, a powdered resin. For example a powdered modified phenol-formaldehyde condensate, as found on the market under the name of "Paranol" may be mixed with aluminum or bronze powder. When mixed at the time of use with nothing more than a common solvent such as mineral spirits merely by stirring it forms a liquid coating composition. We understand that "Paranol" is a phenol-formaldehyde condensate modified with an abietic triglyceride ester gum. The ester gum serves as a thickener for the resin when the combination is

ultimately placed in solution and when properly combined with the resin it also serves to make a better binder for the metallic powder.

The chemical formula for the modified resin "Paranol" is not known to us and so far as we know has never been determined. In common with the resins mentioned below it is believed to have a very complex formula. The various resins mentioned herein, however, are readily obtainable on the market under the names herein given. The methods of condensation of these resins are not claimed herein as part of the present invention. In order that those skilled in the art may further identify these resins, we have indicated them by general chemical terms and where they are modified we have described the modifying agent. In the case of the product "Paranol", it may be substantially duplicated by a process described below. In describing this process we do not intend to indicate that each of the resinous products herein mentioned is prepared in the same manner. We simply cite the process mentioned in order to give a further understanding of a method of preparing this substance directly from its ingredients.

We prefer to purchase "Paranol" on the market but a phenol-formaldehyde condensate modified with ester gum having properties substantially identical with "Paranol" can be prepared as follows: Take 30 parts by weight of phenol crystals, and 20 parts by weight of hexamethylene-tetramine, and heat at 90° C. for about 1½ hours until development of bubbles of water occurs. Prior to the complete condensation of the phenol and hexamethylene-tetramine, melt 25 parts by weight of the ester gum and add it all at once with constant stirring until it becomes homogeneous. The condensation being completed, the mass is then allowed to cool. This mass is substantially identical in properties with "Paranol" on the market.

As an example of the composition of our invention, we take 40 parts by weight of "Paranol", 0.9 part by weight of paradichlorbenzene, and 20 parts of aluminum powder. The "Paranol" is finely ground, preferably to 70 mesh. The aluminum powder comes on the market in a finely ground state. The three are mixed together and as such constitute the dry base which may be sold, shipped and stored as such. When this base is prepared for use it is mixed with a volatile vehicle material to constitute a brush or sprayable liquid. For example, we mix with it approximately 60 parts by weight of mineral spirits having a boiling point of about 160° C. The "Paranol" acts as a thickener and is a gum or modified resin which when once powdered remains in the powdered condition and has little or no tendency to cake together with the aluminum to form a lump, as many other substances might. This property enables the composition other than the metallic powder to be dissolved rapidly in the mineral spirits, when and in the quantities desired, and at the place of use. It serves as a binder in the applied coating. The paradichlorbenzene acts as a leveling agent and aids in the production of a more flexible film. It is also a plasticizer. Its properties are more fully discussed below.

As indicated above "Paranol" is a modified phenol-formaldehyde condensate. Other resins which have suitable physical and mechanical properties may be employed in place of "Paranol". For some purposes we prefer a combination of petroleum resin and indene resin as shown in Example A below. The petroleum resin employed in the example is manufactured by Dayton Synthetic Chemicals, Inc., Dayton, Ohio, and comes on the market as T & H resin No. 200. The manufacturer states that this resin has an acid value of about 0.1 and 0.3, a saponification value of about 5 to 15, iodine value ranging from 130 to 140, and a melting point of about 103 to 108° C. It is a condensation and polymerization of unsaturated hydrocarbons, such as diolefines, cracked oils, etc. Indene resin is described by the manufacturers Neville Chemical Company, Pittsburgh, Pa., as a polymerized indene. The resin employed is Neville Hard Resin, melting point 135° C. The resin is believed to be properly classifiable as a polymerization of coal tar naphtha unsaturated hydro-carbons, the polymerization being produced in the presence of sulfuric acid as a catalyst. In using the mixture of petroleum and indene resins they are powdered separately to a fineness of approximately 100 mesh and then are mixed in with the aluminum powder in the proportions specified below, after which the product is packed for shipment. When prepared for use the product is mixed with coal tar naphtha, gasolene or turpentine, in the proportions given below. We have also used a modification of aroclor resin which is a chlorinated diphenyl. Such modification is described in our copending application Ser. No. 636,012, filed October 3, 1932.

We have also employed in place of the ones just mentioned "Mowilith" and "Vinylite", which are polymerization products of vinyl chloride and vinyl acetate which occur as resins; Styrol resin or "Resoglaz" which is a polymerized styrene $C_6H_5.CH:CH_2$, modified with "Cumar"; "Teglac" which is "Glyptal" modified with rosin; "Amberol" which is a cresylic acid condensate with an aldehyde, modified with tung oil acid; "Lewisol" which is an ester gum, being a condensate of abietic acid and glycerine; "Ellisol" which is a urea-phenol-formaldehyde resin modified with an ester gum. We also may employ natural resins having suitable properties such as Kauri gum.

In employing the various synthetic resins mentioned above or others it is important that they be employed in the state prior to that where the resin becomes infusible and insoluble, usually designated as the "C" stage. It is also important, in these metallizing compositions including aluminum and bronze powders, that resins with a low acid number be employed. Resins with a high acid number tend to interfere with the leveling of the particles to produce a continuous bright metallic film.

Other formulae which we prefer to employ using the resins just mentioned, are as follows:—

Example A

	Parts
Powdered petroleum resin (T & H #200)	25
Powdered indene resin	75
Aluminum powder	46

As a suitable solvent, mix for use with 115 parts coal tar naphtha, gasolene or turpentine.

Example B

	Parts by weight
Powdered modified Aroclor resin	40
Aluminum powder	20
Powdered para-dichlorobenzene	2.5

As a suitable solvent we have used 60 parts by

volume mineral spirits, boiling point about 160° C.

Other formulae which we have used with success are

Example C

	Parts
Powdered Aroclor resin	10
Powdered "Paranol" resin	20
Powdered petroleum resin	70
Aluminum powder	46

As a suitable solvent, mix for use with 100 parts petroleum naphtha.

Example D

	Parts by weight
Powdered "Vinylite" resin	10
Aluminum powder	5

As a suitable solvent we have used 20 to 25 parts by volume of acetone.

Example E

	Parts by weight
Powdered "Teglac"	10 to 15
Aluminum powder	5 to 15

As a suitable solvent we have used 30 parts by volume of acetone.

Example F

	Parts by weight
Powdered "Amberol"	10
Aluminum powder	5

As a suitable solvent we have used 20 to 25 parts by volume mineral spirits, boiling point about 100° C.

Example G

	Parts by weight
Powdered "Ellisol"	10
Aluminum powder	5
Powdered para-dichlorobenzene	0.1

As a suitable solvent we have used 20 to 30 parts by volume of alcohol.

Example H

	Parts by weight
Powdered "Lewisol"	10
Aluminum powder	5
Powdered para-dichlorobenzene	0.1

As a suitable solvent we have used 20 to 30 parts by volume of turpentine.

Example I

	Parts by weight
Powdered modified "Resoglaz"	10
Aluminum powder	5
Powdered para-dichlorobenzene	0.1

As a suitable solvent we have used 20 parts by volume of turpentine.

Example J

	Parts by weight
Powdered "Aroclor" resin	10
Powdered East India gum	10
Aluminum powder	10

As a suitable solvent, mix for use with 30 parts coal tar naphtha.

Example K

	Parts by weight
Powdered natural Kauri gum	10
Aluminum powder	1.8

As a suitable solvent we have used 25 parts by volume of denatured alcohol.

The above proportions are about 2 parts by weight of resin to 1 part by weight of aluminum powder. 3.5 to 5 pounds of the mixture (depending on the fineness of the powder and the solubility of the gum) may be used to advantage per gallon of finished mixture ready for application.

An important characteristic of the resins mentioned in the preferred and other examples above is that they may be powdered and will preserve such powdered form when mixed with aluminum or other metallic powder. In the above examples bronze powder may be substituted in whole or in part for aluminum powder.

The fineness to which the resins are powdered depends upon their ease of solubility. Rapidly soluble resins like "Paranol" and petroleum resin need only be ground to 60 or 70 mesh, while slowly soluble resins like "Vinylite" and Styrol should be powdered to 100 mesh or finer. The different types of resins require different types of common solvents in many instances. Other resins or like materials having properties similar to those set forth in the examples may be used in the place of those set forth therein. In place of the solvents mentioned above other solvents having similar properties may also be used. The solvent ethyl acetate may be substituted in whole or in part.

Paradichlorbenzene is a leveling agent. We have found that other materials containing benzene radicals such as coal-tar-naphtha, benzol, toluol and xylol act as leveling agents. Small proportions of these materials may be added in each of the above examples if desired. The paradichlorbenzene also acts as a plasticizer and serves to produce dried paint films which are highly flexible.

The metallic powder and resins in the above formulae constitute the more necessary components of a dry base to which the solvent, etc. is added at the point of use. The base containing also the binder, etc. is a substantially complete finely ground metallic powder coating material and is miscible at the time of use with the necessary solvent. When the solvent is added a liquid metallic powder coating composition is obtained which may be applied to various surfaces in the manner customary for application of such material. The coating produced thereby is exceptionally bright and lasting. The metal becomes largely suspended by mere agitation when the liquid medium is added and much of it remains about at the surface of the film so as to give a bright and lustrous metallic film which to the naked eye is continuous.

In the examples and claims herein, the expression "metallic powder" is employed as referring to bronze and aluminum powders. These powders are sometimes referred to as bronze and aluminum flakes. By the expression "powder", we intend to include also the flake material.

The formulae in the examples above are adapted for use on average surfaces. When used on porous substances such as wall-board, wood, plaster, brick-work, etc. the binder will be absorbed by the porous material tending to carry away some of the binder. For this work therefore it is desirable to use a somewhat larger proportion of binder and on non-porous metal surfaces it may be desirable to use a smaller proportion of binder, as will be clear to anyone skilled in the art. Under novel conditions preliminary trials may be desirable to adjust these proportions to give the most brilliant and lasting results.

While we have described our base components as in finely powdered form it is obviously possible though not generally desirable to prepare the

powder base in tablets, cakes, or briquettes held together by a readily soluble material which may be either the binder, thickener, the leveler, or all these. Such a preparation does not, however, depart from the purpose and spirit of the invention because it may be easily broken up by the solvent when finally added and agitated therewith. When, therefore, we say finely powdered we mean in the preparatory sense of thorough commingling of the fine particles of binder, thickener, leveler, and/or any one of these adapted to act as described upon the addition of solvent at the place and time of use.

The expression "synthetic resin material" as used in the claims is intended to include both unmodified synthetic resin as well as synthetic resin modified as herein described.

While we have described our improvements in great detail and with respect to preferred forms thereof, we do not desire to be limited to such details and forms since many changes and modifications may be made and the invention embodied in widely different forms without departing from the spirit and scope thereof in its broader aspects. Hence we desire to cover all modifications, forms and embodiments coming within the language or scope of any one or more of the appended claims.

What we claim as new and desire to secure by Letters Patent, is:

1. A dry powdered base for a metallic coating composition smoothly miscible by stirring at ordinary temperature with an organic solvent such as naphtha, turpentine, alcohol or other ordinary paint solvent at the time of application, containing a fine metallic powder and a modified phenol formaldehyde condensate soluble in said solvent in the proportion of approximately one of powder by weight to two of condensate by weight capable of remaining in easily miscible condition on storage and capable on solution of producing a paint having suitable properties for application to steel and other structures.

2. A dry powdered base for a coating composition according to claim 1 including para-dichlorbenzene.

3. A dry powdered base for a metallic coating composition smoothly miscible by stirring at ordinary temperature with an organic solvent such as naphtha, turpentine, alcohol or other ordinary paint solvent at the time of application, containing a fine metallic powder and a finely powdered synthetic resin material soluble in said organic solvent in the proportion of approximately one of metallic powder by weight to two of synthetic resin material by weight, said resin material serving in at least one of the following ways:—as a binder, a thickener and to give a leveling action; said base remaining in easily miscible condition on storage and capable on solution of producing a paint having suitable properties for application to steel and other structures.

4. A dry powdered base for a metallic coating composition smoothly miscible by stirring at ordinary temperature with an organic solvent such as naphtha, turpentine, alcohol or other ordinary paint solvent at the time of application, containing a fine metallic powder and a finely powdered synthetic resin modified by an ester gum soluble in said organic solvent in the proportion of approximately one of metallic powder by weight to two of modified synthetic resin by weight, said resin serving in at least one of the following ways:—as a binder, a thickener and to give a leveling action, said base remaining in easily miscible condition on storage and capable on solution of producing a paint having suitable properties for application to steel and other structures.

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