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ORGANO METALLIC PROTECTIVE AGENT

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10 Claims. (Cl. 134—79)

This invention relates to a process for improving the durability of coating compositions on exposure to sunlight, and more particularly to a process for increasing the resistance of nitrocellulose to the action of ultra-violet light.

It is well known that nitrocellulose is sensitive to the action of ultra-violet radiation present in sunlight and that its value in coating compositions is limited thereby. Several months of summer exposure is sufficient to completely destroy clear nitrocellulose films. Prior to the present invention no practical method has, insofar as I am aware, been disclosed for retarding this destructive action of sunlight on nitrocellulose lacquer films.

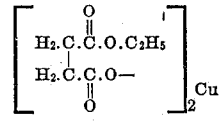
While some metallic organic salts have been incorporated in nitrocellulose films, these salts were simply for the purpose of serving as a filler or for the purpose of imparting a color to the film that will not fade upon exposure to visible or ultra-violet light. The present invention, on the other hand, resides in the discovery that the organic salts of a certain group of metals when incorporated in nitrocellulose under the proper conditions and in certain proportions will substantially prevent the transmission of ultra-violet light through the film and thereby prevent the deterioration of the film because of the damaging effect of the ultra-violet rays.

This invention has as an object the improvement of the resistance of nitrocellulose films to ultra-violet light. A further object is the preparation of nitrocellulose coating compositions durable on exposure to sunlight.

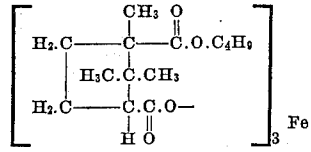
These objects are accomplished by incorporating with the nitrocellulose organic salts of various metals capable of absorbing the destructive radiation present in sunlight and thus retarding the deleterious action of this radiation on nitrocellulose. These agents comprise organic salts in which the metallic radical is such as to confer good absorption of the ultra-violet light and in which the organic radical is capable of providing solubility of the metallic salt in organic solvents and compatibility with the nitrocellulose. I have found that the metals iron, copper and cobalt when combined with suitable organic radicals are effective retarders of ultra-violet light transmission through nitrocellulose films.

By compatible salts is meant those salts which are compatible with the dried film as well as with the nitrocellulose solution used for the production of the coating composition. Compatible salts, therefore, produce a clear homogeneous film with the nitrocellulose; are soluble in the same solvents and diluents as the nitrocellulose, and do not have any deleterious effect on the dried film.

I have found that the metal salts of aliphatic acids provide valuable agents for protecting nitrocellulose films against the destructive action of ultra-violet light, provided the metal in the salt is selected from the group of metals referred to, namely; iron, copper and cobalt. The agents selected from this class of compounds may be of widely different chemical structure, such as the succinates and camphorates as:

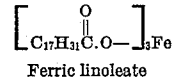


Copper ethyl succinate

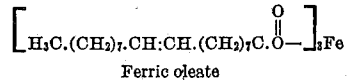


Ferric butyl camphorate

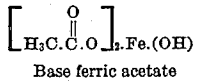
Embraced within the metal salts of the aliphatic acids are also the very valuable protective agents furnished by the metallic salts of the fatty acids, as the metallic salts of the drying oil acids, i. e., linseed oil acids and China-wood oil acids; the metallic salts of the semi- and non-drying oil acids, i. e., castor oil acids and cotton seed oil acids. Specific examples of these compounds are:



Ferric linoleate



Ferric oleate



Base ferric acetate

The nitrocellulose is used in the form of a 20–25% solution in suitable solvents. A typical nitrocellulose base solution for this purpose may be made according to the following formula:

	Percent
Ethyl acetate	25.0
Butyl acetate	20.0
Toluol	20.0
Denatured alcohol	10.0
Nitrocellulose	25.0

Other lacquer constituents may be added such as natural gums, polyhydric alcohol-polybasic acid resins, softeners or pigments.

To this lacquer mixture is then added the organo-metallic salt, preferably dissolved in toluene, butyl alcohol, or other suitable solvent.

In the following examples, I have indicated the method of employing these agents in clear lacquers and the increase in durability that may be obtained by their use. The durability data were obtained by exposing panels coated with the lacquers at an angle of 45° from the vertical position and facing due south.

Example 1

100 g. of the nitrocellulose base containing 25 g. of nitrocellulose is mixed with a solution containing 10 g. of ferric linoleate dissolved in toluol. This lacquer gives reddish brown, durable films. A film of this type applied over an enameled surface withstood outdoor weathering for 140 days, as compared with 50 days for an ordinary lacquer film comprising nitrocellulose, a natural gum, and softener.

Example 2

100 g. of nitrocellulose base containing 25 g. of nitrocellulose is mixed with a solution containing 5 g. of the ferric salt of castor oil acids. Films prepared from this lacquer are reddish brown in color. A film of this type applied over an enameled surface lasted 120 days during outdoor exposure, as compared with 50 days for a lacquer containing nitrocellulose, a natural gum, and softener.

The effectiveness of the organo metallic salts in increasing the resistance of nitrocellulose to sunlight is proportional to their opacity to ultra-violet light. The following table shows the ultra-violet light transmission values of films containing various protective agents.

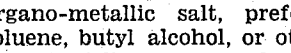
Ultra-violet transmission

Agent	Percentage transmission	
	2800–3600 A.U.	3130 A.U.
	Percent	*Percent*
Ferric linoleate	2.8	2.6
Ferric linoleate	0.8	0.0
Copper ethyl succinate	16.6	9.0
Ferric ethyl succinate	0.5	0.0
Ferric butyl camphorate	3.4	1.5
Cobalt control (no agent)	55.0	53.0

The above results were obtained on clear lacquer films having a thickness of 0.00100+0.00005 inch. The ratio of protective agent, nitrocellulose and softener in the films was 1–4–2, with the exception of the second listing of ferric linoleate which was 2–4–2.

When the agent for retarding the transmission of ultra-violet light is the metal salt of an organic acid having more than one carboxylic group as succinic acid, one of the carboxyl groups is esterified as indicated in the compound mentioned because the presence of the alkyl group lends solubility to the compound.

I have discovered that the ferric, copper and cobalt salts of the class of compounds comprised by the alicyclic carboxylic acids furnish highly effective protective agents. In these compounds the carboxylic ring does not contain the conjugate double bonds which characterize the true aromatic compounds. The agents within this class are exemplified by the salts of naphthenic acid, sometimes referred to as a hexahydro aromatic acid. Examples of this class of compounds are: ferric naphthenate,



and the salts of the resin acids, particularly the resinates and abietates which are especially valuable for the purposes of the present invention. The resinates were formed from rosin which contains the several acids known as the resin acids and the abietates were formed from abietic acid, one of the acids contained in rosin. The following table shows the ultra-violet transmission of films containing members of this class of agents.

Ultra-violet transmission of nitrocellulose lacquer films

Film thickness=0.00100″

Protective agent		Transmission percentage	
		2800–3600 A.U.	3130 A.U.
		Percent	*Percent*
Ferric resinate	1/4/2	0.25	0.0
Ferric abietate	1/4/2	10.2	6.1
Ferric abietate	2/4/2	3.9	1.4
Copper abietate	1/4/2	16.5	4.5
Copper abietate	2/4/2	9.1	1.2
Cobalt abietate	1/4/2	5.3	1.3
Cobalt abietate	2/4/2	0.8	0.2
Ferric naphthenate	1/4/2	2.9	1.0
Control (no agent)		55.0	53.0

The ratio of the agent to the nitrocellulose and softener is indicated in the second column above.

In the tables indicating the percentage transmission, the wave length range of 2800–3600 A. U. used in testing the ultra-violet transmission of the film embraces the entire wave length range contained in sunlight which is considered to be effective in decomposing nitrocellulose films. The radiation of wave length 3130 A. U. is considered to be particularly effective in decomposing nitrocellulose films.

The selection of the organic salts of the metals mentioned as agents for the retardation of ultra-violet light is based upon the solubility of the salt and on its compatibility with the nitrocellulose film. All metals will not confer to the organic compounds the property of rendering nitrocellulose films opaque or substantially so to ultra-violet light. Zinc butyl phthalate, for instance, exercises no protective influence in preventing deterioration of nitrocellulose by ultra-violet light. Other metals that I have incorporated into nitrocellulose films in the form of their organic salts are: K, Mg, Al, Cr, Mn, Ni, Zn, Zr, Cd, Sn, Ba, Hg, Pb, Bi, Th, U and Nd. Some of these metals are wholly ineffective for the purposes of the present invention; and the salts of those metals that do retard the transmission of ultra-violet light through the film, do so insufficiently, even when incorporated in as large a quantity as is feasible. These metals not tested are too rare and expensive, or they lie so far on the acid side of the periodic table that they probably would not form stable salts. While each of the operative metals mentioned have more than one valence, they are generally used in their ordinary or most stable state of valence. For instance, cobalt and copper are used in the divalent state and iron in the trivalent state. Although some of the metals, such as iron, may be

introduced in a lower state of valence, oxidation occurs to convert the metal to its state of higher valency, and it is in this form that these agents are most satisfactory.

When the metals are combined with suitable organic radicals, to form agents compatible with the nitrocellulose film, other than those mentioned, the percentages of ultra-violet transmission are not appreciably changed when the various agents are used in the necessary proportion to make the metal effective as a retarder of the transmission of ultra-violet light through the film.

The proportion of the metallic derivative to be incorporated will vary with the degree of durability required and the particular derivative employed; other factors being equal, the higher the metallic content of the derivative used, the greater in general will be the degree of protection afford against ultra-violet light. As a general indication it may be stated that in manufacturing clear nitrocellulose lacquers, I prefer to introduce a sufficient quantity of the organo-metallic salt to confer upon the dried lacquer film almost complete opacity to the most harmful ultra-violet radiation present in sunlight. For the best results the transmission should not exceed 10% at 3130 A. U. and should not exceed 25% for the entire range in sunlight. In the case of the most effective agents, it is sufficient to use 3 parts of the agent to 12 parts of nitrocellulose. Too much of the metal salt gives water sensitive films. It is therefore not usually practicable to use more than one part of agent with one part of nitrocellulose.

The present process for improving the durability of nitrocellulose has proved particularly valuable in the case of clear nitrocellulose lacquers. In the case of enamels, opacity to ultra-violet light is obtained by the presence of the pigment, and hence the addition of the agents described above do not have as marked an effect in retarding light decomposition. It is likely, however, that these agents would be effective in improving the durability of nitrocellulose plastics and may be particularly advantageous in laminated glass, the connecting nitrocellulose film of which is known to deteriorate in sunlight.

The process of improving the durability of nitrocellulose films by the incorporation of organo-metallic salts is particularly advantageous because it can be accomplished without sacrifice in the drying-time or hardening rate of the lacquer film. Nitrocellulose lacquers containing oil-modified polyhydric alcohol-polybasic acid resins show fair durability, but are slower drying than nitrocellulose itself. The incorporation of materials of the type disclosed in this invention, has little or no effect on the drying rate and leads to a lacquer having much better durability than the slower drying lacquers containing oleo-resinous materials.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A composition comprising nitrocellulose and a nitrocellulose-compatible metal salt of an alicyclic carboxylic acid of the class consisting of naphthenic acid and resin acids, the metal in said salt being selected from the group consisting of iron and cobalt, said salt being present in an amount sufficient to protect a film of the composition from deterioration by ultra-violet light.

2. A composition comprising nitrocellulose and a nitrocellulose-compatible metal salt of a resin acid, the metal in said salt being selected from the group consisting of iron and cobalt, said salt being present in an amount sufficient to protect a film of the composition from deterioration by ultra-violet light.

3. A composition comprising nitrocellulose and a metal salt of abietic acid, the metal in said salt being selected from the group consisting of iron and cobalt, said salt being present in an amount sufficient to protect a film of the composition from deterioration by ultra-violet light.

4. A composition comprising nitrocellulose and, in amount sufficient to protect a film of the composition from deterioration by ultra-violet light, ferric resinate.

5. A composition comprising nitrocellulose and, in amount sufficient to protect a film of the composition from deterioration by ultra-violet light, ferric abietate.

6. A coating composition comprising nitrocellulose and a nitrocellulose-compatible metal salt of an alicylic carboxylic acid of the class consisting of naphthenic acid and resin acids, the metal in said salt being selected from the group consisting of iron and cobalt, and the salt being present in an amount sufficient to reduce the transmission of ultra-violet light by a clear film of the composition .001'' thick to less than 25% at 2800–3600 A. U. and less than 10% at 3130 A. U. and sufficient to protect a film of the composition from deterioration by ultra-violet light.

7. A coating composition comprising nitrocellulose and a nitrocellulose-compatible metal salt of a resin acid, the metal in said salt being selected from the group consisting of iron and cobalt, and the salt being present in an amount sufficient to reduce the transmission of ultra-violet light by a clear film of the composition .001'' thick to less than 25% at 2800–3600 A. U. and less than 10% at 3130 A. U. and sufficient to protect a film of the composition from deterioration by ultra-violet light.

8. A coating composition comprising nitrocellulose and a metal salt of abietic acid, the metal in said salt being selected from the group consisting of iron and cobalt, and the salt being present in an amount sufficient to reduce the transmission of ultra-violet light by a clear film of the composition .001'' thick to less than 25% at 2800–3600 A. U. and less than 10% at 3130 A. U. and sufficient to protect a film of the composition from deterioration by ultra-violet light.

9. A coating composition comprising nitrocellulose and ferric resinate, the ferric resinate being present in an amount sufficient to reduce the transmission of ultra-violet light by a clear film of the composition .001'' thick to less than 25% at 2800–3600 A. U. and less than 10% at 3130 A. U. and sufficient to protect a film of the composition from deterioration by ultra-violet light.

10. A coating composition comprising nitrocellulose and ferric abietate, the ferric abietate being present in an amount sufficient to reduce the transmission of ultra-violet light by a clear film of the composition .001'' thick to less than 25% at 2800–3600 A. U. and less than 10% at 3130 A. U. and sufficient to protect a film of the composition from deterioration by ultra-violet light.

HAMILTON BRADSHAW.

CERTIFICATE OF CORRECTION.

Patent No. 1,962,132. June 12, 1934.

HAMILTON BRADSHAW.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 54, last line of boxed table should not appear as one line as shown in the patent, it should appear as shown below:

Cobalt Control (no agent).....	55.0	53.0

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of July, A. D. 1934.

Bryan M. Battey

(Seal) Acting Commissioner of Patents.