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DECORATED METAL SHEET AND VARNISH
THEREFORFrank R. Stoner, Jr., and Daniel M. Gray,
Sewickley, Pa., assignors to Stoner-Mudge, Inc.,
Pittsburgh, Pa., a corporation of PennsylvaniaNo Drawing. Application October 2, 1940,
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This invention relates to an improved finishing varnish for use over resin- and oil-base lithographic color coatings on metal, and finds particular application in the coating of decorated tins, lithographed cans, printed metal closures and similar metallic surfaces partially or totally covered with lithographic color coatings. It relates specifically to a finishing varnish consisting of a copolymer of a vinyl halide and a vinyl ester, modified with a copolymer of a vinyl halide, a vinyl ester, and maleic acid, maleic anhydride or a lower aliphatic ester of maleic acid as hereinafter particularly set forth, together with a suitable plasticizer, the whole being dispersed in a solvent for the vinyl copolymers.

In a previous application, filed August 22, 1940, Serial No. 353,652, we have described the application of an improved finishing varnish to printed paper surfaces. We have experimented further, and have extended the utility of our improved finishing varnishes into the field of metal decorating, in the manner hereinafter fully described.

The process of decorating metal involves the application of an organic coating to the metal; this may be a varnish, a lacquer, a lithographic print, a solid color coat or combinations of these. We are here concerned with decoration of metal only by means of solid color coatings and lithographic "prints" of an oleoresinous nature. The general practice in decorating metal in this manner is to first apply a thin coat of a sizing varnish which may be a pure synthetic resin, an oil-modified resin of the polybasic acid-polyhydric alcohol type, an oleoresinous varnish of the kauri gum-China-wood oil type, a dammar spirit varnish, or like material. The primary requirements of such size coats are relative freedom from color, a fair degree of elasticity, a high degree of adhesion to the metal, and the ability to form a satisfactory bond with the subsequently applied color and finish coats. The size coat is ordinarily applied at film weights ranging from 0.5 to 2.0 milligrams per square inch of dry film. They may be baked at temperatures ranging from 200–400° F. for periods of time of 10–30 minutes.

Following the size coat there is applied a base color coat, generally comprising an oleoresinous vehicle pigmented with the usual inorganic pigments or with organic colors such as lakes, toners, or oil- and resin-soluble dyes. This base color coat is baked at 200–300° F. for periods of time of 15–40 minutes, depending upon the heat stability of the particular pigments or dyes employed.

The metal sheet is next printed by a lithographic process, usually by the so-called "offset" process, whereby one or more colored ink patterns are applied from rolls. The usual practice

is to bake each ink print separately, though the application of several colors at once using a multi-color press may be carried out on large production runs of a single item. In this case the several ink prints may all be baked in one operation. Past practice has been to employ lithographic inks based on unmodified drying oils as vehicles, typically heavy-bodied linseed oil. Also currently employed as ink vehicles are heat-converting resins of the oil-modified polybasic acid-polyhydric alcohol type.

The final step in metal decorating usually involves the over-all application of a suitable finishing varnish for purposes of protection and also to enhance the gloss of the ink prints. In special cases the baking of the ink prints may be dispensed with, and the finishing varnish applied directly over the undried inks, after which the so coated metal sheet is given a final bake to set up the finishing varnish, the heat of this bake being sufficient to convert or "set" the underlying ink prints.

The usual finishing varnishes are of oleoresinous type, employing natural fossil resins "heat run" with drying oils, typically linseed and China-wood oil. These varnishes dry or "set" primarily by oxidation and polymerization; accordingly a high degree of temperature and relatively long exposure to these elevated temperatures are necessary for complete drying.

The requirements of a completely satisfactory finishing varnish are that it shall be colorless, odorless, resistant to "after-yellowing" in the dark or in sunlight, and resistant to water and steam, and to alcohols and mild chemicals such as dilute acids and alkalis. The varnish film should be flexible and ductile, possess high gloss, have extreme abrasion- and mar-resistance, and be tightly adherent to the lithographed color and ink coatings and to the size. The varnish must be capable of being applied from rolls without ridging; it must be formulated in solvents which will not soften, lift or blur the undercoats; and it must be capable of admixture with surface-blooming waxes to provide self-lubrication in subsequent stamping and forming operations carried out on the coated metal sheet. The present commercially available finishing varnishes are seriously deficient in resistance to after-yellowing in the dark, tend to darken on exposure to direct sunlight, lack abrasion- and mar-resistance, are readily attacked by water, steam, solvents and even mild alkali, and are not initially free from color and odor.

It is an object of our invention to produce a finishing varnish possessing all of the desirable properties specified above, and possessing in marked degree the properties of superior adhesion and abrasion or mar resistance. Another object of our invention is to produce a finishing

varnish having unusual grease resistance, high resistance to oils and petroleum hydrocarbons, to water, and to mild acids and alkalis. A further object of our invention is to produce a highly flexible, tightly adhered varnish film on lithographed metal surfaces without the necessity of employing the extreme baking temperatures usually required for "setting" chemically resistant varnishes.

We have found that the above objects may be attained in high degree by employing as the film-forming components of our finishing varnish a mixture of (1) a copolymer of a vinyl halide and a vinyl ester of a lower aliphatic monocarboxylic acid, and (2) a copolymer of a vinyl halide, a vinyl ester of a lower aliphatic monocarboxylic acid, and maleic acid, maleic anhydride, or a lower alkyl ester of maleic acid.

For convenience, the term "lower" will be used throughout the specification and claims to designate aliphatic radicals containing no more than 6 carbon atoms. Thus, by "vinyl ester of a lower aliphatic monocarboxylic acid" we mean vinyl acetate, vinyl propionate, vinyl butyrate, and the higher aliphatic homologs containing up to 6 carbon atoms in the alkyl group attached to the esterifying carboxyl group. By "lower alkyl esters of maleic acid" we mean the methyl, ethyl, propyl, butyl, and higher homologous alkyl esters of maleic acid containing up to 6 carbon atoms in the esterifying alkyl groups.

The polymers and copolymers of vinyl halides and vinyl esters are well known. They result from the conjoint polymerization of a vinyl halide, typically vinyl chloride, with a vinyl ester of a lower aliphatic monocarboxylic acid, typically vinyl acetate, usually in the presence of a suitable solvent for the monomeric starting materials, and a peroxide catalyst. We have found that the copolymers of vinyl chloride and vinyl acetate are particularly suited for our purposes as component (1), and we advantageously employ copolymers in which the percentage of vinyl chloride lies between 65% and 95% by weight, the percentages of vinyl acetate being correspondingly 35% and 5%.

Several preferred compositions for component (1) are as follows:

	Percent by weight
(a) Vinyl chloride.....	80
Vinyl acetate.....	20
(b) Vinyl chloride.....	87
Vinyl acetate.....	13
(c) Vinyl chloride.....	85
Vinyl acetate.....	15

For convenience we shall hereafter refer to these copolymers which form our component (1), as "vinyl halide-vinyl ester copolymers."

The mixed copolymers of vinyl halides, vinyl esters of lower aliphatic monocarboxylic acids, and maleic acid derivatives, which we use as our component (2), are not so widely known. They result from the conjoint polymerization of vinyl halides and the previously described lower aliphatic vinyl esters, together with a minor proportion of maleic acid, maleic anhydride or a lower aliphatic ester of maleic acid. (A typical copolymer involving only vinyl chloride and maleic aliphatic esters is described in United States Letters Patent 2,187,817, for example.) We have found that copolymers of vinyl chloride, vinyl acetate, and maleic anhydride are particularly suitable for our component (2), though we may

advantageously employ copolymers containing maleic acid and lower aliphatic maleic esters in place of the maleic anhydride. We have found it desirable to employ copolymers in which the percentage of vinyl chloride lies between 65% and 94% by weight, the remainder being vinyl acetate and maleic derivative. Thus the percentage of vinyl acetate will be reduced by the amount of maleic derivative present, which will ordinarily lie between 0.2% and 5.0% by weight, based on maleic anhydride. By simple molecular weight ratios it is obvious that a "maleic content" of 1%, based on the anhydride, is equal to 1.18% of maleic acid, to 1.33% of monomethyl maleic ester, to 1.47% of dimethyl ester, to 1.47% of monoethyl ester, and to 1.76% of diethyl ester, for example. Throughout the specification and claims, it will be understood that percentage figures for "maleic content" are based on maleic anhydride; conversion to equivalent percentage of other maleic derivatives is a simple calculation.

Several preferred compositions for component (2) are as follows:

(d) Vinyl chloride.....	percent by weight	85.0
Vinyl acetate.....	do	13.0
Di-methyl maleic ester.....	do	2.0
(e) Vinyl chloride.....	do	70.0
Vinyl acetate.....	do	28.7
Maleic anhydride.....	do	1.3
(f) Vinyl chloride.....	do	65.0
Vinyl acetate.....	do	34.2
Maleic acid.....	do	0.8
(g) Vinyl chloride.....	percent	87.0
Vinyl acetate.....	do	11.8
Maleic anhydride.....	do	1.2

For convenience we shall hereafter refer to these maleic-modified copolymers which form our component (2), as "maleic-modified vinyl halide-vinyl ester copolymers."

It is important that the degree of polymerization of the copolymers of components (1) and (2) be controlled within fairly close limits. The degree of polymerization may not be too low, to the end that unstable, brittle, relatively soft and pervious copolymers be not formed; the degree of polymerization may not be too high, to the end that insoluble or only sparingly soluble, rubbery, non-adherent copolymers be not formed. We advantageously employ copolymers having molecular weights in the range of 5,000 to 20,000 as determined by the familiar Staudinger viscosity method, and prefer to employ these in the range of 8,000 to 14,000. Our preferred materials have absolute viscosities as shown in the accompanying table, determined on 18% solutions in pure methyl isobutyl ketone.

Resin component	Absolute viscosity range (centipoises at 20° C.)
(1).....	90-130
(2).....	80-140

All attempts to use unmodified vinyl halide-vinyl ester formulations as finishing varnishes over the usual lithographic prints on metal have been commercially unsatisfactory. While adequate chemical and abrasion resistance has been obtainable with such simple varnishes, provided sufficiently heavy films are employed, the known poor adhesion of such unmodified coatings renders them commercially valueless. Previous

investigators have attempted to overcome this fatal deficiency by increasing the baking temperature; their efforts proved useless, in that such elevated temperatures were destructive of the underlying inks and even of the unmodified vinyl resin film. This lack of adhesion is particularly manifested over the printed portions of the lithographed metal, so that while reasonably adequate adherence to the non ink-containing portions of the coated surface may be had, that portion of the film lying over the ink is so poorly adhered that it may be stripped off with ease.

In an effort to improve the degree of adhesion, we have experimented widely. Various admixtures with other resins compatible with the vinyl halide-vinyl ester resins were tried. Thus we have employed admixtures with oil-modified and non-oil modified polybasic acid polyhydric alcohol resinoids familiarly known as alkyds, nitro-cellulose and other cellulose esters such as cellulose acetate, cellulose acetate-propionate and cellulose acetate-butyrate, ethyl cellulose, various natural and synthetic compatible waxes, phenol-aldehyde condensation products and the like. While the degree of adhesion was in a few cases slightly improved by the addition of these substances, the improvement was in no case of sufficient magnitude to have commercial possibilities, or if so, other undesirable qualities such as decreased mar resistance, hardness and flexibility resulted.

Additions of the maleic-modified vinyl halide-vinyl ester copolymers which we previously described and herein specifically disclose as our component (2) showed, however, a spectacular improvement in the degree of adhesion produced, and this without the necessity of increasing the bake temperature and without sacrifice of the other desirable properties associated with vinyl halide-vinyl ester films. Our experiments show that blends containing as little as 10% by weight of component (2) give appreciable improvement in adhesion of our finishing varnish film. We find that the percentage of maleic modified vinyl halide-vinyl ester constituent may be as great as 40% of the resinous portion without too marked a decrease in the desirable properties of the resulting film. Our preferred composition, however, contains 25% by weight of the maleic-modified vinyl halide-vinyl ester component, and 75% of the unmodified vinyl halide-vinyl ester component. Higher percentages of component (2) do not appear to give a corresponding increase in adhesion, and the abrasion resistance tends to be lowered. Amounts of component (2) less than 25%, while showing improvement in adhesion, are not consistently satisfactory over all lithographed metal surfaces. The optimum amount of component (2) appears to be 25%, based on a large number of experiments over various types of printing inks and sizing varnishes.

Finally, we have attempted preparation of suitable finishing varnishes from maleic-modified vinyl halide-vinyl ester copolymers alone. Such varnishes yield films which are unsatisfactory from a commercial standpoint. Stability is poor; abrasion resistance is seriously deficient; the moisture resistance is inferior to that of most of the familiar oleoresinous finishing varnishes. It is apparent that only in the blends of our invention are the desirable properties of high degree of adhesion, excellent abrasion and mar resist-

ance, coupled with inertness to atmospheric oxidation, acid and alkali resistance, freedom from odor and color, and moisture impermeability combined. And these properties are obtained in our finishing varnish films employing baking temperatures not exceeding 275° F. for 10 minutes in contrast to the appreciably more drastic baking schedules necessitated in commercial practice with prior art varnishes.

The formulation of our improved finishing varnishes offers no difficulty. We prefer to employ high boiling aliphatic ketones as solvents, typically methyl amyl ketone, cyclohexanone, methyl propyl ketone, and methyl isobutyl ketone. Other suitable solvents such as butyl acetate, mesityl oxide, isophorone and chlorinated aromatics may be employed if desired. As diluents we prefer to use aromatic hydrocarbons such as toluol, xylol, hiflash naphtha, tetrahydronaphthalene, decahydronaphthalene and their homologs. For certain types of application the addition of an added plasticizer to further increase the normally satisfactory flexibility of our improved varnish film may be desirable. For this purpose we employ with advantage any of the familiar plasticizers which are compatible with the vinyl resins. Typical of such materials are tricresyl phosphate, dibutyl phthalate, diamyl phthalate, di(butoxyethyl) phthalate, triphenyl phosphate, phenyl-dixenyl phosphate, castor oil and the like. The concentration of plasticizer is preferably about 25% by weight, based on the total non-volatile content.

The application of our improved finishing varnish offers no difficulties. Thus it may be applied by the usual roll coating machines, or it may be applied by simply brushing or dipping. We prefer to bake the varnish coat for 10 minutes at 250° F. This schedule insures complete removal of volatile solvents and gives improved gloss. Higher baking temperatures are possible, but lead to no useful gain in final properties, and may be deleterious to the underlying prints. Thus we have prepared satisfactory varnished metal sheets, for example, using baking schedules between 10 and 30 minutes at temperatures ranging from 200° F. to 400° F. The optimum schedule appears to be 10 minutes at 250° F. based on a large number of experiments over a variety of inks and size coats.

The following exemplary formulations will serve to illustrate our invention, it being understood that we are not limited to the specific compositions or proportions therein disclosed. All of the percentages are on a weight basis.

Example I

60	(1) Copolymer of vinyl chloride.....	85.0%	} 22.5%
	vinyl acetate.....	15.0%	
	(2) Copolymer of vinyl chloride.....	87.0%	} 7.5%
	vinyl acetate.....	11.7%	
	maleic anhydride.....	1.3%	
	Cyclohexanone.....		70.0%
			100.0%

Example II

70	(1) Copolymer of vinyl bromide.....	65.0%	} 23.3%
	vinyl acetate.....	35.0%	
	(2) Copolymer of vinyl chloride.....	65.0%	} 5.7%
	vinyl propionate.....	30.0%	
	diethyl maleic ester.....	5.0%	
	Tricresyl phosphate.....		7.2%
	Methyl amyl ketone.....		63.8%
			100.0%

Example III

(1) Copolymer of vinyl chloride.....	90.0%	12.0%
vinyl butyrate.....	10.0%	
(2) Copolymer of vinyl bromide.....	70.0%	8.0%
vinyl acetate.....	28.5%	
maleic acid.....	1.5%	5.0%
Diamyl phthalate.....		
Isophorone.....		7.5%
Methyl isobutyl ketone.....		15.0%
Methyl amyl ketone.....		7.5%
Hiflash naphtha.....		45.0%
	100.0%	

Example IV

(1) Copolymer of vinyl chloride.....	87.0%	18.0%
vinyl acetate.....	13.0%	
(2) Copolymer of vinyl chloride.....	87.0%	2.0%
vinyl acetate.....	12.0%	
maleic acid.....	1.0%	40.0%
Methyl amyl ketone.....		
Xylol.....		40.0%
	100.0%	

Example V

(1) Copolymer of vinyl chloride.....	87.0%	15.0%
vinyl acetate.....	13.0%	
(2) Copolymer of vinyl chloride.....	87.0%	5.0%
vinyl acetate.....	11.8%	
maleic anhydride.....	0.2%	65.0%
dimethyl maleic ester.....	1.0%	
Methyl amyl ketone.....		15.0%
Hiflash naphtha.....		
	100.0%	

Example VI

(1) Copolymer of vinyl chloride.....	87.0%	15.0%
vinyl acetate.....	13.0%	
(2) Copolymer of vinyl chloride.....	87.0%	5.0%
vinyl acetate.....	12.0%	
maleic anhydride.....	1.0%	8.0%
Methyl ethyl ketone.....		
Methyl isobutyl ketone.....		16.0%
Isophorone.....		8.0%
Xylol.....		48.0%
	100.0%	

The percentages by weight of components (1) and (2) based on the total resin content in the six examples are given in the following table:

Example	Component (1)	Component (2)
	Per cent	Per cent
I.....	75.0	25.0
II.....	80.0	20.0
III.....	60.0	40.0
IV.....	90.0	10.0
V.....	75.0	25.0
VI.....	75.0	25.0

Examples I, V and VI represent preferred compositions; Examples II, III and IV are satisfactory but not necessarily preferred.

Having described our invention, and having pointed out the advantages attendant on its use, We claim as our invention:

1. A finishing varnish for application to dec-

orated metal sheet comprising (1) a copolymer of a vinyl halide and a vinyl ester of a lower aliphatic monocarboxylic acid, and (2) a copolymer of a vinyl halide, a vinyl ester of a lower aliphatic monocarboxylic acid, and a substance selected from the group consisting of maleic acid, maleic anhydride and the lower alkyl esters of maleic acid, and (3) a solvent for the whole composition.

2. The composition of claim 1 in which the resinous components consist of (1) 60 to 90 parts by weight of the vinyl halide-vinyl ester copolymer, and (2) 40 to 10 parts by weight of the maleic-modified vinyl halide-vinyl ester copolymer.

3. The composition of claim 1 in which the resinous components consist of (1) 60 to 90 parts by weight of a copolymer of vinyl chloride and vinyl acetate in which the weight percentage of the vinyl chloride lies between 65 and 95, the remainder being vinyl acetate; and (2) 40 to 10 parts by weight of a copolymer of vinyl chloride, vinyl acetate, and a maleic derivative selected from the group consisting of maleic acid, maleic anhydride, and the lower alkyl esters of maleic acid, in which the weight percentage of the vinyl chloride lies between 65 and 94, that of the maleic derivative between 0.2 and 5.0, the remainder being vinyl acetate.

4. A metal article coated with a sizing varnish, a lithographic varnish, and a finishing varnish baked on at a temperature not exceeding 275° F. comprising (1) 75 parts by weight of a copolymer of vinyl chloride (87%) and vinyl acetate (13%), and (2) 25 parts by weight of a copolymer of vinyl chloride (87%), vinyl acetate (11.5%) and a maleic derivative selected from the group consisting of maleic acid, maleic anhydride, and the lower aliphatic esters of maleic acid (1.5%).

5. A metal article coated with a sizing varnish, a lithographic varnish, and a baked-on finishing varnish comprising (1) 60 to 90 parts by weight of a copolymer of a vinyl halide and a vinyl ester of a lower aliphatic monocarboxylic acid, and (2) 40 to 10 parts by weight of a copolymer of a vinyl halide, a vinyl ester of a lower aliphatic monocarboxylic acid, and a substance selected from the group consisting of maleic acid, maleic anhydride and the lower alkyl esters of maleic acid, in which the baking schedule for the finishing varnish does not exceed 275° F. for 10 minutes.

FRANK R. STONER, JR.
DANIEL M. GRAY.