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METHOD OF REMOVING PAINT, VARNISH, AND LACQUER FILMS FROM SURFACES

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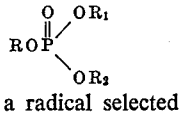
This invention relates to a method of removing paint, varnish and lacquer films from surfaces; more specifically, this invention relates to an improved method of removing paint, varnish and lacquer films from surfaces utilizing a composition containing an alkyl diaryl phosphate ester having the formula



wherein R represents a radical selected from the group consisting of alkyl and alkoxyethyl radicals containing from 1 to 12 carbon atoms and R_1 and R_2 are each selected from the group consisting of phenyl and cresyl radicals.

The paint, varnish and lacquer removing compositions heretofore employed generally contained volatile and highly flammable organic solvents such as benzene, toluene and acetone which render the use of such compositions exceedingly hazardous from a flammability standpoint. It has been further found that the vapors which are evolved during the use of such compositions are frequently irritating to the mucous membrane, and the liquids contained in such compositions are frequently quite toxic, injurious to the skin and have disagreeable odors. These compositions also usually contain paraffin wax or other waxes for the purpose of retaining the volatile active ingredients on the painted surface during the paint softening operation. The subsequent removal of the softened paint from wood surfaces by scraping or other means tends to leave a residue of wax on the treated articles from which the coating is being removed. This wax film is not readily removable by water and frequently resists complete removal by means of gasoline or a similar solvent. This wax residue is frequently responsible for poor adhesion of new paint subsequently applied to the surfaces. Moreover, the new paint film tends to stay sticky and to resist hardening in the presence of the wax film. When such compositions are utilized in removing paint from wood surfaces, it has been found that quite frequently a raising of the grain results.

One of the objects of this invention is to provide a method of removing paint, varnish and lacquer films from surfaces utilizing a composition which is characterized by the absence of waxes and other normally solid or semi-solid constituents.

Another object of this invention is to provide a method of removing paint, varnish and lacquer films from surfaces utilizing a composition characterized by non-toxicity and non-flammability thereby eliminating many of the hazards incidental to the paint removing compositions heretofore employed.

Further objects will become apparent from the description of the novel process of this invention.

It has now been discovered that paint, varnish and lacquer films may be softened in a relatively short time by applying thereto a composition containing one or more of the alkyl diaryl phosphate esters previously described. According to the novel process of this invention, therefore, paint, varnish and lacquer films are removed from a surface containing said films by applying thereto a composition containing one or more of these alkyl diaryl phosphate esters, allowing the composition to remain on the surface until the paint, varnish or lacquer film is loosened, and then removing the loosened film by suitable mechanical means, such as by scraping the surface with a scraping tool or by rubbing the surface with steel wool. After the paint, varnish or lacquer film has been removed from the surface, the residual composition containing the alkyl diaryl phosphate ester may then be removed quite readily from the surface by washing the treated area with water. Quite frequently the paint, varnish or lacquer film is so significantly loosened by treatment with the aforementioned compositions containing one or more of these alkyl diaryl phosphate esters, that flushing the surface with water is all that is required to completely remove the film. After the treated surface has dried, it may be repainted with full assurance that the resulting painted surface will dry properly and result in a hard, tack free surface.

The following examples are illustrative of the use of compositions containing an alkyl diaryl phosphate ester, as previously described, in removing paint, varnish and lacquer films:

Removal of paints from metal

One side of a steel strip was covered with an aluminum paint while the other side was covered with a titanium-base paint. A thin film of a composition containing an alkyl diaryl phosphate ester, as above described, was then applied to these strips and the effect of such compositions upon the painted surfaces noted. The results are indicated in Table A wherein are set forth the various compositions utilized and the time of contact between the composition and the painted surfaces necessary to permit a sufficient softening of the film to permit complete removal of the paint by mechanical means.

TABLE A.—REMOVAL OF PAINTS FROM METALS

Example	Remover, Composition by Weight	Exposure Time, hrs.	Remarks Removal of Paint with Putty Knife
I	2-ethylhexyl diphenyl phosphate, 50% 2-ethylhexyl dicresyl phosphate, 50%	2.0	Completely removed.
II	6-methylheptyl diphenyl phosphate, 50% 3,5,5-trimethylhexyl diphenyl phosphate, 50%	2.0	Do.
III	methyl diphenyl phosphate, 75% ethyl diphenyl phosphate, 25%	1.0	Do.
IV	butyl diphenyl phosphate, 90% n-dodecyl diphenyl phosphate, 10%	1.5	Do.
V	ethyl diphenyl phosphate, 70% tetrachloroethylene, 30%	1.5	Do.
VI	6-methylheptyl diphenyl phosphate, 50% tetrachloroethylene, 50%	1.5	Do.
VII	n-dodecyl diphenyl phosphate, 40% trichloroethylene, 60%	1.5	Do.
VIII	butyl diphenyl phosphate, 60% 99% isopropanol, 40%	1.0	Paint so loose it was removed by flushing metal with stream of water.
IX	2-ethylhexyl diphenyl phosphate, 60% 99% isopropanol, 40%	1.0	Completely removed.
X	2-ethylhexyl diphenyl phosphate	1.5	Do.
XI	2-ethylhexyl dicresyl phosphate	2.0	Do.
XII	methyl diphenyl phosphate	1.0	Do.
XIII	ethyl diphenyl phosphate	1.0	Do.
XIV	6-methylheptyl diphenyl phosphate	1.5	Do.
XV	n-dodecyl diphenyl phosphate	2.5	Do.
XVI	butyl diphenyl phosphate	1.0	Do.
XVII	butoxyethyl diphenyl phosphate	1.0	Do.
XVIII	benzoxyethyl diphenyl phosphate	4.0	Do.

Removal of paints from wood

Two varieties of samples were tested. One type is designated as "red paint" and the other as "green paint." The wood strips covered with "red paint" had two coats of primer consisting of aluminum paint and one coat of "red paint," the principal ingredient of the latter being iron oxide. The strips of wood covered with "green paint" had two coats of a white paint, the pigment being titanium oxide, and one coat of "green paint," wherein the main pigment was lead chromate. Except for the titanium-base paint, the vehicle for the other paints was mainly an alkyd varnish.

A thin film of a composition containing an alkyl diaryl phosphate ester, as previously described, was applied to the painted surface of each of these wood strips. The composition was applied as indicated in Table B. The effect of these compositions upon the painted surface is set forth in Table B.

nish was quite soft. The syrupy mass was removed from the surface with a putty knife after 12 hours' exposure. After the surface was scraped free of softened varnish, the wood was wiped with a cloth, wet with turpentine. The same surface, without further treatment, was then brushed with varnish about 48 hours after wiping with the turpentine-wet cloth. About 10 hours after the varnish had been applied, the surface was hard and dry.

Alkyl diaryl phosphate esters as brush softeners

All of the paint brushes utilized in the following test contained pure pig bristles set in vulcanized rubber. To prepare the brushes for this test, the brushes were saturated with paint and the paint allowed to harden by aging.

TABLE B.—REMOVAL OF PAINTS FROM WOOD

Example	Color of Test Board	Remover, Composition by Weight	Application Method	Exposure Time, hrs.	Remarks
I	Red	2-ethylhexyl diphenyl phosphate, 50%; 2-ethylhexyl dicresyl phosphate, 50%	Brushed on	0.25	Essentially no action.
				1.0	Paint removed to aluminum primer.
				3.0	Difficult to remove aluminum paint with putty knife.
				4.0	Aluminum paint removed with steel wool.
II	do	n-dodecyl diphenyl phosphate, 50%; n-dodecyl dicresyl phosphate, 50%	do	0.25	Same as above.
				1.0	
				3.0	
				4.0	
III	do	2-ethylhexyl phenyl cresyl phosphate, 100%	Cotton Wad	0.25	Same as above.
				0.75	
				3.0	
				4.0	
IV	do	butyl diphenyl phosphate, 50%; butoxyethyl diphenyl phosphate, 50%	Brushed on	1.0	Paint fairly soft.
				1.5	Removed red paint with putty knife.
				2.5	Aluminum primer removed with steel wool.
V	do	methyl diphenyl phosphate, 40%; butyl diphenyl phosphate, 60%	do	1.0	Paint fairly soft.
				1.5	Removed red paint with putty knife.
				2.5	Aluminum primer removed with steel wool.
VI	do	butyl diphenyl phosphate, 90%; n-dodecyl dicresyl phosphate, 10%	Cotton Wad	1.0	Same as above.
				1.5	
				2.5	
VII	Green	2-ethylhexyl diphenyl phosphate, 50%; 2-ethylhexyl dicresyl phosphate, 50%	Brushed on	0.25	Essentially no action.
				1.0	Paint quite soft.
				4.0	Down to wood with putty knife.
VIII	do	n-dodecyl diphenyl phosphate, 50%; n-dodecyl dicresyl phosphate, 50%	do	0.25	Same as above.
				1.0	
				4.0	
IX	do	2-ethylhexyl phenyl cresyl phosphate	Cotton Wad	0.25	Essentially no action.
				0.75	Considerable softening.
				4.0	Complete removal of paint with putty knife.
X	do	butyl diphenyl phosphate, 50%; butoxyethyl diphenyl phosphate, 50%	Brushed on	1.0	Most of paint removed.
				1.5	Complete removal with putty knife.
XI	do	methyl diphenyl phosphate, 40%; butyl diphenyl phosphate, 60%	do	1.0	Almost complete removal.
				1.5	Complete removal of paint with putty knife.
XII	do	butyl diphenyl phosphate, 90%; n-dodecyl dicresyl phosphate, 10%	Cotton Wad	1.0	Paint fairly soft.
				1.5	Complete removal of paint with putty knife.

After removal of the painted surface in each of the tests described in Table B, each board was wiped vigorously with a cloth well soaked with turpentine. Then the board was wiped with a dry cloth and allowed to dry at room temperature. When dry, the boards were repainted. Half of these boards were given an undercoat of aluminum paint and the other half painted with a white paint (main pigment—cryptone). As a final coat, all boards were painted with a lead-base blue enamel. Drying of the enameled surface was satisfactory in all cases.

Removal of varnish from wood

A 15-year old varnished surface was covered with a mixture of 2-ethylhexyl diphenyl phosphate and 2-ethylhexyl dicresyl phosphate (equal portions by weight). The phosphate ester mixture was applied with a brush.

After a few hours the surface was softened considerably. To show the non-volatile nature of the "remover," the treated surface was allowed to stand for seven days after the first application of the ester. The syrupy mass was then removed with a putty knife thereby effecting a complete removal of the varnish film.

A 15-year old varnished surface was brushed with a 60:40% by weight mixture of tetrachloroethylene and ethyl diphenyl phosphate. After about one hour the varnish was quite soft. The syrupy mass was removed from the surface with a putty knife after 12 hours' exposure. After the surface was scraped free of softened varnish, the wood was wiped with a cloth, wet with turpentine. The same surface, without further treatment, was then brushed with varnish about 48 hours after wiping with the turpentine-wet cloth. About 10 hours after the varnish had been applied, the surface was hard and dry.

Alkyl diaryl phosphate esters as brush softeners

All of the paint brushes utilized in the following test contained pure pig bristles set in vulcanized rubber. To prepare the brushes for this test, the brushes were saturated with paint and the paint allowed to harden by aging.

Several paint formulas were used to saturate the brushes. These formulas were as follows:

Formula No. 1—"Black enamel":
- Pigment — Carbon black.
- Vehicle — Oils and resins. Volatile thinner.

Formula No. 2—"White paint":
- Pigment 52.6%—
  - Cryptone — 82.0%.
  - TiO_2 — 3.6%.
  - Talc — 14.4%.
- Vehicle 47.4%—
  - Varnish — 85.0%.
  - Drier and thinner — 15.0%.

Formula No. 3—"Blue enamel":
- Pigment 42%—
  - Sublimed lead — 90%.
  - TiO_2 — 10%.
- Vehicle 58% Tinted with Ultramarine Blue—
  - Linseed oil — 19.5%.
  - Tung oil — 17.4%.
  - Resins — 12.8%.
  - Japan drier — 4.6%.
  - Mineral spirits — 41.5%.
  - Turpentine — 4.2%.

Formula No. 4—"Lacquer" — Commercial linoleum lacquer.

Formula No. 5—"Varnish":
- Resins — 27%.
- Vegetable oils — 24%.
- Mineral spirits — 49%.

After the brushes had been thoroughly soaked in these

various paint, varnish and lacquer formulas, and the composition allowed to harden with aging in the open, the brushes were immersed in a composition containing an alkyl diaryl phosphate ester, and the ability of this composition to soften and permit complete removal of the paint, varnish or lacquer formulation noted. The results are set forth in Table C.

TABLE C.—ALKYL DIARYL PHOSPHATES AS BRUSH SOFTENERS

Brush No.	Paint Formula	Saturated Brush Aged for Time	Softening Agent, Composition by Weight	Remarks
1	1	ca. 2 months	2-ethylhexyl diphenyl phosphate, 50% 2-ethylhexyl dicresyl phosphate, 50%	Brush was softened in 18 hours, washed with water and then reused as 1A. 1A was first used to paint a metal surface satisfactorily with paint Formula 2, then used as 1A.
1A	2	do	2-ethylhexyl diphenyl phosphate, 50% 2-ethylhexyl dicresyl phosphate, 50%	Brush was softened and ready for washing with water in 2.5 hours.
2	2	1 week	2-ethylhexyl diphenyl phosphate, 50% 2-ethylhexyl dicresyl phosphate, 50%	Brush was softened and ready for washing with water in 2.5 hours.
3	3	ca. 2 months	n-dodecyl diphenyl phosphate, 50% n-dodecyl dicresyl phosphate, 50%	Brush was softened and ready for washing with water in 2.5 hours.
4	4	do	2-ethylbutyl diphenyl phosphate, 50% 2-ethylbutyl dicresyl phosphate, 50%	Brush was softened and ready for washing with water in 2.5 hours.
5	5	do	methyl diphenyl phosphate, 75% ethyl diphenyl phosphate, 25%	Brush was softened and ready for further treatment in 1 hour. Because varnish is not completely soluble in this mixture, the brush was first immersed for a few minutes in turpentine and then washed with water.

The alkyl diaryl phosphate esters, as previously described, are characterized by low volatility and exceptionally low flammability. The physical properties of many of the phosphate esters which may be utilized in the novel process of this invention are set forth in Table D.

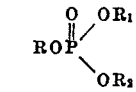
TABLE D.—PHYSICAL PROPERTIES

Ortho-Phosphate Ester	Sp. Gr., 25°/25° C.	$N_D^{25°}$	Pour Point, ° F.	Flash Point, ° F.	Fire Point, ° F.
Methyl diphenyl phosphate	1.2315	1.5355	>−70	410	480
Ethyl diphenyl phosphate	1.1984	1.5279	>−70	395	470
Ethyl dicresyl phosphate	1.1467	1.5248			
Butyl diphenyl phosphate	1.1512	1.5190	>−70	405	475
Butoxyethyl diphenyl phosphate	1.1484	1.5130	−60	450	530
2-Ethylbutyl diphenyl phosphate	1.1217	1.5152	>−70		
2-Ethylbutyl dicresyl phosphate	1.0879	1.5135			
n-Hexyl diphenyl phosphate	1.1172	1.5135	>−70		
2-Ethylhexyl diphenyl phosphate	1.090	1.510	<−65	420	460
2-Ethylhexyl dicresyl phosphate	1.0645	1.510	−55	425	485
2-Ethylhexyl phenyl p-cresyl phosphate	1.0785	1.5082	−60		
6-Methylheptyl diphenyl phosphate	1.0903	1.5076	<−65	405	485
n-Octyl diphenyl phosphate	1.0843	1.5062	−70	460	520
Benzoxyethyl diphenyl phosphate	1.2092	1.5528			
3,5,5-trimethylhexyl diphenyl phosphate	1.0748	1.5050			
n-Decyl diphenyl phosphate	1.0627	1.5025	>−70	485	520
2-Ethylhexoxyethyl phenyl cresyl phosphate	1.0795	1.5020			
n-Dodecyl diphenyl phosphate	1.0402	1.4987	−10	420	505
n-Dodecyl dicresyl phosphate	1.025	1.5008	−45	440	510

In addition to these physical properties, these phosphate esters are characterized by low toxicity. The novel process of this invention, therefore, provides a means of removing paint, varnish and lacquer films wherein the toxicity and flammability hazards have been substantially eliminated. Due to the relatively low volatility of these alkyl diaryl phosphate esters, it is not necessary to employ any waxy materials in the paint removing compositions in order to retain the active ingredient on the painted surface during the paint softening operation. Utilizing the novel process of this invention, therefore, results in a wax-free surface.

As indicated in the preceding examples, the alkyl diaryl phosphate esters previously described may be utilized as the sole active ingredient in the paint removing composition or mixtures of various phosphate esters may be utilized. Furthermore, if desired, these phosphate esters may be mixed with other materials having some utility as paint removing ingredients. Typical of such additional agents which may be utilized are the various alkyl alcohols, trichloroethylene, tetrachloroethylene, etc. It is to be emphasized, however, that the use of such additional agents is not necessary for the purpose of this invention and, in fact, if used in too great a quantity, may detract from the desirable properties of the composition imparted thereto by these alkyl diaryl phosphate esters.

Any of the alkyl diaryl phosphate esters having the formula



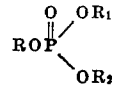
wherein R represents a radical selected from the group consisting of alkyl and alkoxyethyl radicals containing from 1 to 12 carbon atoms and R_1 and R_2 are each selected from the group consisting of phenyl and cresyl radicals may be utilized in the novel process of this invention. The alkyl and alkoxyethyl radicals as used in the above described formula, throughout the specification and in the claims, may be unsubstituted or substituted with one or more substituent radicals which do not deleteriously affect the desirable non-toxicity, stability, or non-corrosive properties of the particular phosphate ester. Typical of such substituent radicals are the hydroxyl radicals, alkoxyethoxy radicals, aryl radicals, such as the phenyl radical, and the substituted aryl radicals, such as the cresyl radical. These alkyl diaryl phosphate esters have been found to be particularly unique in the process of this invention as tricresyl phosphate or other liquid triaryl phosphates have been found to be ineffectual as paint removers because of their relatively slow softening action. Such triaryl phosphate esters are also considerably more toxic than the alkyl diaryl phosphate esters utilized in this process. Tri(2-ethylhexyl) phosphate has also been found to be essentially useless in such an application because of its exceptionally slow softening action. The lower trialkyl phosphates are too unstable hydrolytically, resulting in corrosion problems when their use in removing paint from metals is attempted.

The novel process of this invention has been found to be effective in the removal of aged paint, varnish, lacquer, enamel or resin films and newly applied or partially aged films. The process is applicable to the treatment of both

metal and wood surfaces, as well as to the removal of paint, lacquer and varnish from other substances, for example, wool, cotton waste and textiles. Among the types of coatings removed from metal and wood surfaces by means of the novel process of this invention are those containing cellulose esters, such as cellulose nitrate and cellulose acetate; cellulose ether, such as ethyl cellulose; phenol aldehyde resin coatings; varnishes including those containing rubber; paints formulated with white lead, barium sulfate, zinc sulfide or titanium oxide pigments and various oils, such as linseed oil, tung oil, oiticica oil and others; vinyl resin, melamine aldehyde resin, urea formaldehyde resin coatings, etc.

What is claimed is:

1. A process for the removal of paint, varnish and lacquer films from surfaces bearing said films comprising applying to said surfaces a film softening amount of a substantially non-inflammable fluent alkyl diaryl phosphate ester having the formula



wherein R represents a radical selected from the group consisting of alkyl and alkoxyethyl radicals containing from 1 to 12 carbon atoms and R_1 and R_2 are each selected from the group consisting of phenyl and cresyl radicals, allowing said composition to remain on said surface until said film is loosened, and removing the loosened film.

2. A process as described in claim 1 wherein the alkyl diaryl phosphate ester is ethyl diphenyl phosphate.

3. A process as described in claim 1 wherein the alkyl diaryl phosphate ester is butyl diphenyl phosphate.

4. A process as described in claim 1 wherein the alkyl diaryl phosphate ester is butoxyethyl diphenyl phosphate.

5. A process as described in claim 1 wherein the alkyl diaryl phosphate ester is 2-ethylhexyl diphenyl phosphate.

6. A process as described in claim 1 wherein the alkyl diaryl phosphate ester is 2-ethylhexyl cresyl phenyl phosphate.

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