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PROCESS FOR PRESERVING PAINT IN STORAGE

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This invention relates to paint compositions, and relates particularly to inhibitors or anti-skinning agents in drying oil compositions such as paints, lacquers, varnishes and enamels.

In the manufacture of preparations containing oxidizable substances, especially those containing drying oils, such as varnishes, enamels and especially ready mixed or prepared paints, difficulty has been encountered due to the fact that upon prolonged standing in the can in which the drying oil composition, especially a ready mixed paint is packaged, the air in the unfilled portion of the can in cooperation with the necessary dryers in the oil or paint produces a highly objectionable skin upon the surface of the oil or paint, and in some instances tends to convert the paint into a thick, jelly-like mass which is practically useless.

The present invention utilizes a small proportion of certain complex, organic, phenolic compounds obtained from certain petroleum fractions as constituents in prepared paints, which by their presence modify the interaction of the drying oils and drying agents to prevent both skinning in the can, and gelling of the drying oil or paint compound in the can. In addition, these phenolic compounds modify the action and interaction of the drying agent and the drying oils in the paint, to produce a smoother, more elastic, more durable paint coating after the paint has been applied to the surface to be covered.

In the manufacture of paints, varnishes, enamels, and film protective coating compounds, it is customary to include in the prepared paint composition a suitable, and substantial, quantity of an oxidation catalyst, commonly known as a "dryer" to increase the drying rate of the oil, so that the paint, varnish or enamel will dry hard to the touch in a relatively short time, a much shorter time than that in which the normal drying oils would dry in the absence of such an oxidation catalyst. These "dryers" which are customarily salts of lead, manganese, and cobalt accelerate the oxidation of the drying oil to produce the desired hard, protective film, but in addition they produce various other phenomena which are objectionable, such as cracks, roughness, brittleness, etc., in the dried paint film, a tendency to weather rapidly, to peel from the support, and in some instances a tendency towards a general breakdown of the film structure.

Thus the commercial development of quick-drying paints, varnishes, enamels, etc., has been seriously handicapped and retarded by the tendency of the paint, varnish, and enamel compositions to change their fluid consistency during storage, and to gel and produce surface skin while in storage, either in a closed container, or when the container cover is removed and the paint compound exposed to the air, thereby limiting to relatively short periods of time the intervals during which the material can be kept in storage, and limiting to a very short interval, the time during which the container may be left uncovered. Furthermore, paint compounds which dry with the rapidity required by workers in the art do not have the strength, elasticity and durability of slower drying coating compounds since they weather rapidly, crack, dry with a rough surface, are unduly brittle, and tend to peel from the support. These disadvantages are due in part to the necessity of cooking the drying oil, and to the manner in which the cooking is conducted, since if the oil resin mixture is cooked for too long a period, a gel structure in the dried oil may be produced of a type which does not weather satisfactorily, and of a type which does skin prematurely during storage in a container.

The petroleum phenol compounds of the present invention in a paint, varnish or enamel composition control the gel structure, modify the catalytic effect of the dryer, and alter the film character of the dried compound in such fashion as to avoid substantially all of these above mentioned difficulties, without increasing the drying time.

Thus an object of the invention is to compound a paint, varnish or enamel with a dryer substance to increase the drying rate, and with a petroleum phenol compound to modify the effect of the dryer on the drying oil to increase the strength, smoothness, and toughness of the film without increasing the drying time, and at the same time avoid gelling in the can, and avoid the production of surface skins upon the paint compound while in the container.

Other objects and details of the invention will be apparent from the following description:

In the refining of petroleum oil, a substantial portion of the crude petroleum is "topped" to remove the lower boiling hydrocarbons which boil within the gasoline range, and the "topped" crude is "cracked" for the production of additional quantities of gasoline boiling range hydrocarbons. A residual, heavy petroleum fraction boiling at temperatures above the gasoline boiling range remains. This is suitable for a fuel oil stock but before shipment for such use, it is commonly treated with a strong, aqueous, caustic solution. This treatment produces from the heavy

petroleum fraction, a dark, viscous material which is insoluble in the aqueous caustic, but which settles out of the heavy fraction along with the excess caustic forming a three layer system of which the upper layer is the purified fuel oil stock; the intermediate layer consists of crude sodium phenate salts; and the bottom layer is the surplus aqueous caustic soda solution. These layers are separated and the top heating oil layer is in purified form ready for shipment and use. The bottom, caustic solution, layer is suitable for reuse in the washing and purification of further portions of heavy fraction. The middle layer contains crude sodium salts of the desired phenate compounds. These crude compounds are washed with petroleum ether or naphtha to remove residual hydrocarbons, and the crude salts are then treated with carbon dioxide or a dilute mineral acid in sufficient quantity to combine with the sodium of the phenate salts and liberate only the desired phenols, any naphthenic acid salts present being kept wholly undecomposed in the solution. The liberated phenols are then separated from the solution and purified by distillation, preferably under reduced pressure, or by blowing with air. If still higher purity is desired, the phenols may be redistilled under vacuum. The boiling range of the phenols so obtained is usually substantially higher than the boiling range of the petroleum fraction from which they are obtained. By gas treatment and redistillation the phenolic compounds can readily be freed from hydrocarbons and other impurities such as the naphthenic acids.

The following detailed procedure may be utilized for the recovery of the pure phenols.

Example 1

A sample of acid treated heating oil from cracked East Texas crude was contacted in an agitator with 0.15 pound per barrel of 40° Bé. caustic soda. Three layers were formed, of which the bottom layer was a caustic soda solution which could be reused, the intermediate layer, dark in color, contained the phenols, and the top layer was the caustic-washed oil. These layers were separated and the intermediate layer was extracted three times with 10% by volume of naphtha and then acidified with either carbon dioxide or dilute acid for the precipitation of the phenols. Approximately 0.16% of crude phenols, based on the heating oil treated, were obtained. Inspections of these crude phenols were as follows:

Gravity—API	6.8
Color (Robinson)	Black
Percent water	20

Distillation—A. S. T. M.	°C.
Initial boiling point	98.9
5% off at	102.2
10% off at	102.2
20% off at	110.0
30% off at	218.3
40% off at	230.6
50% off at	238.9
60% off at	250.0
70% off at	265.0
80% off at	284.4
90% off at	Cracked
95% off at	Cracked

The crude phenols were then vacuum distilled, the initial boiling point being about 30° C. at 5 mm. pressure. Various cuts were taken off up to about 240° C. at 5 mm. pressure; the residue remaining in the still was a hard, tar-like solid. A sample of such phenols was fractionated and refractionated three times, the following fractions of the specified carbon hydrogen proportions being obtained in the last fractionation:

Fraction	Boiling range, °C., at 2 mm. pressure	Percent C	Percent H
1	30–70		
2	70–80		
3	80–90	78.7	9.06
4	90–100	78.89	9.36
5	100–110		
6	110–120	78.98	9.55
7	120–130	79.38	9.35
8	130–140		
9	140–150	79.6	9.23
10	150–160		
11	160–170	79.99	9.3
12	170–180		
13	180–210	80.86	8.87

The petroleum phenols may be characterized as containing a total of about 9 to 23 carbon atoms per molecule with about 3 to 17 of these carbon atoms present in saturated hydrocarbon groups, which show a hydrogen deficiency as compared to the hydrogen content of straight-chain alkyl groups. This deficiency of hydrogen can be ascribed to the presence of cyclo-aliphatic hydrocarbon groups. Thus, while the saturated hydrocarbon substituents of petroleum phenols may be considered as paraffinic, they do not have the paraffinicity of simple alkyl groups. Moreover, analysis of fractions of these phenolic substances shows that they contain more oxygen than could be accounted for by the phenolic group, as can be seen from the following analytical data:

A sample of petroleum phenols was fractionated into four portions and the following cuts obtained:

Fraction	Boiling range, °C.	Percent C	Percent H	Percent O (By difference)
1	85–120 at 6 mm.	79.09	9.06	11.85
2	120–130 at 6 mm.	79.35	9.16	11.49
3	130–140 at 6 mm.	78.19	8.82	12.99
4	140–150 at 6 mm.	80.66	8.54	10.80

Fraction 3 on further analysis was found to contain more oxygen as shown by the following analysis:

Percent carbon	78.19
Percent hydrogen	8.82
Probable empirical formula	$C_{12}H_{16}O_{1.5}$
Molecular weight (calc.)	184
Molecular weight (found)	190.3
Sap. No. of acetylated product (calc.)	340
Sap. No. of acetylated product (found)	256.67

It can be seen that if the oxygen atoms were phenolic, the acetylated product would have a saponification number of 340 mg. of KOH/gm. If only one of the oxygen atoms per molecule were phenolic the saponification number would be 246 which is in reasonable agreement with the value of 256 as found in the analysis.

In the case of heavier distillates, such as lubricating oil and heavier oils, the use of aqueous alkali solutions does not remove all of the phenolic bodies and it is necessary to treat with an alcoholic solution of strong alkali. Solvents other than monohydric alcohols (methyl, ethyl, isopropyl alcohols, etc.) may be used; e. g. glycols, glycerols, polyglycols, dioxane, glycol or glycerol mono-esters, or similar substances.

Excessive amounts of water should be avoided in such solvents, that is, only sufficient water should be added so that the solvent and the petroleum hydrocarbons readily separate. In some instances, 5% of water will be sufficient. The amount of alkali employed should vary from 3 to 15% or more of the amount of solvent used, depending upon the concentration of the phenolic products and the type of stock being treated. About 1 to 10% by volume (on the oil treated) of the total solvent is generally used in the extraction. The preferred temperature is room temperature, although temperatures as low as —30° C. and up to 100° C. may be used. Countercurrent extraction is preferable.

The following example illustrates the extraction of phenols from heavy distillates:

Example 2

Heavy Talang Akar kerosene (15 gallons), which has been previously treated with aqueous alkali and which boils substantially above 500° C., is extracted with one-half gallon of methyl alcohol containing one-half pound of potassium hydroxide. The mixture is centrifuged, the alcohol layer is distilled, and upon acidification of the distillation residue 128 grams of crude phenols are recovered. These are vacuum distilled at 5–8 mm. pressure.

The phenolic compounds so obtained are generally liquid mixtures varying in viscosity and boiling point, the values of these properties increasing with increase in boiling point of the petroleum source of material. These phenols contain from about 10 carbon atoms per molecule to 27 carbon atoms or more.

In the higher boiling fractions, there is a deficiency in hydrogen which indicates the presence of more than one nucleus or condensed nuclei.

These petroleum phenols are the substances utilized in the paint composition of the present invention.

The petroleum phenol anti-skinning agents produced as above described may be added to substantially any paint, varnish or enamel compound to obtain the above described advantages in the character and quality of the coating compound of the dried coating. The phenols may be separated into the various cuts as above described, or they may be used in the unseparated state. They may be added to paints in the proportion of from 0.1% of the complete paint compound to approximately 5 to 7% of the complete paint compound depending upon the proportion of drying oil, the proportion of volatile solvent and other characteristics and requirements.

The paint base may consist of practically any of the standard proportions and constituents of oils, pigments, thinners, dryers and the like. The oil base may consist of raw or boiled linseed oil, or tung oil, or lallemantia-seed oil, galeopsis oil, perilla oil, rubber-seed oil, soya bean oil and the various synthetic drying oils.

With these drying oils there may be compounded substantially any of the usual paint pigments such for instance as white lead, lithopone, barytes, the chrome colors including chrome green, chrome yellow, etc., the earth colors including umber and sienna, as well as the lake pigments generally, including such pigments as permolith, titanox, zinc oxide, Gastex black, iron oxide black, maroon oxide, ferric oxide, litharge, lime blue, naphthol green, orange lakes, Turkey red, etc.

Many types of suitable thinners and solvents may likewise be used including such solvents as petroleum naphtha in its various grades, turpentine, petroleum ether, benzine, shale spirits, coal tar naphtha benzene, toluene and the various synthetic solvents commonly employed.

In the preparation of varnishes, as well as paints, practically any of the usual natural varnish gums may be used including Bola, Congo, copal, damar, kauri, Manila, Pontianak, Macassar and Singapore, and the various synthetic resins.

In any of these paint compounds appropriate quantities of dryers may be utilized such as lead, manganese and cobalt, linoleate, naphthenate and resinate.

In addition, the composition includes the petroleum phenols according to the present invention.

In prepared paints, the pigment may be present in the proportion of 10% to 40%; the drying oil may be present in the proportion of 20% to 60%; the thinner may be present in the proportion of 10% to 30%, and the dryer may be present in the proportion of 0.5% to 1 or 2% or even as high as 7%; based on the weight of the drying oil used and as above pointed out, the petroleum phenol anti-skinning agents according to the invention may be present in the proportion of 0.1% to 5 to 7%.

The following series of comparative tests show the superior efficiency of the present anti-skinning agent in paint compositions.

Example 1

A high grade varnish which showed a pronounced tendency toward the production of surface skins upon storage was prepared according to the following formula:

Modified phenolic resin	pounds	100
China-wood oil	gallons	30 (225 pounds)
Petroleum thinner	do	50 (375 pounds)
Dryers:		
Lead salts	pounds	2.8
Manganese salts	do	0.21
Cobalt salts	do	0.07

(The dryers are equivalent to 0.4% lead, 0.03% manganese and 0.01% cobalt based on the weight of drying oil.)

In the preparation of this composition, the oil and 75 pounds of the resin were heated in a varnish kettle to a temperature of 550° F. for a period of 30 minutes. The remaining 25 pounds of the resin were then added and the whole cooled to a temperature of about 450° F. The thick mixture was then thinned with the petroleum thinner and cooled to room temperature. When room temperature was reached, the above indicated amounts of dryers were mixed and stirred thoroughly into the varnish compound.

This varnish as so prepared constituted a very rapid drying varnish which contained approximately 51% of non-volatile matter and such an amount of dryer that when flowed on to a clean wooden panel, the film dried hard to the touch in approximately 3½ hours.

25 gram portions of this finished varnish prepared in the above described manner were then mixed with the petroleum phenols according to the present invention, some of the sample portions being mixed with the various cuts of distilled petroleum phenols; other samples being mixed with the unseparated petroleum phenols, and still other samples being mixed with various

other commercial anti-skinning agents on the market, and still other samples being prepared without any anti-skinning agents.

These 25 gram portions as so compounded were placed in small vials having a capacity of approximately 50 to 60 cc.'s, filling them approximately half full and were then tightly stoppered to exclude further quantities of air. These samples were stored at room temperature and were examined regularly, and a surface skin was considered to have formed when the surface of the vial contents was sufficiently hard to support the varnish when the vials were inverted.

Those samples which did not show a surface skin at the end of four days were supplied with additional air by withdrawing the stoppers at the end of four day intervals.

This particular varnish compound is very bad as far as the production of surface skins is concerned, and in addition storage in half filled containers greatly promotes the formation of surface skins. Accordingly this is an accelerated test which is equivalent to months or years of storage in normally practically filled cans of paints, varnishes, or enamels.

For purposes of comparison the samples prepared included not only specimens of the above-described varnish with the petroleum phenols according to the invention in various forms and proportions, but included also "test blanks" in the form of varnish samples half filling the test vials in the absence of anti-skinning agents of any sort, and also test vials containing samples of the above varnish with various of the standard commercial anti-skinning agents. Of the various available commercial anti-skinning agents, Guiacol is one of the most efficient of the previous known anti-skinning agents. Guiacol is the methyl ether of phenol:

$$C_6H_4(OH)OCH_3$$

This substance has a somewhat disagreeable odor, and also is relatively high in price. In addition quantities greater than about 1% cannot be employed without a serious reduction in drying rate, when the material is added to the quick-drying varnishes or paints and lower percentages such as 0.1% are effective to inhibit the skinning phenomena for only about 20 days storage in the can. Another commercial anti-skinning agent known as "PHO" was also utilized for comparison purposes. This substance is a phenol modified coumarone-indene resin as described in U. S. Patents Nos. 2,077,009 and 2,098,361.

The test results set forth in the following table were obtained from samples of varnish tested as above-described.

Inhibitors	Condition of film after 32 days
Blank (no inhibitor)	Skin.
Guiacol	No skin.
PHO	Bad skin.
Crude petroleum phenol	No skin
Cut No. 1	Do.
Cut No. 2	Do.
Cut No. 3	Do.
Cut No. 4	Do.
Cut No. 5	Do.
Cut No. 6	Do.
Mixture of cuts from 1-6	Do.
Cut No. 7	Do.
Cut No. 8	Do.
Cut No. 9	Do.
Cut No. 10	Do.
Cut No. 11	Do.
Cut No. 12	Do.
Cut No. 13	Do.

These results show the efficiency of the petroleum phenol substances of the invention as anti-skinning agents to protect paint while stored in cans.

The inhibited varnish samples which showed no skinning after standing for 32 days with fresh supplies of air at 4 day intervals, were flowed over a clean wooden panel together with samples of the untreated varnish for purposes of comparison. The inhibited varnish samples when flowed over the panel, allowed to dry, and left exposed to the atmosphere for several weeks showed a smooth, tough, firm film free from any undesirable or detrimental film or surface degradation. In contrast, untreated varnish samples flowed upon a panel and allowed to dry and weather for the same period of time showed pronounced tendencies towards blistering and wrinkling of the film surface. These test panels clearly showed the effect of the anti-skinning agents in avoiding the undesirable oxidation effect which tends to occur in the latter stages of the drying process and by the avoidance of this undesirable tendency, avoided the tendency towards the formation of wrinkles in the film caused by superficial or irregular oxidation through the thickness of the film. Furthermore these effects are markedly superior to the corresponding effects obtained with either of the commercially available anti-skinning agents.

Thus the anti-skinning agents of the invention provide a new, useful and unexpected combination of effects in that they not only avoid the production of skin upon the paint surface in the can, but also avoid the formation of gel-like characteristics either in the can or in the paint film, and in addition equalize and normalize the oxidation and drying effect in the film as well as exerting a marked stabilizing effect upon the drying agents required for rapid drying of the paint film.

The anti-skinning agents according to the invention may be used in practically any type of drying oil composition including paints, varnishes and enamels, etc., as well as in the drying oils themselves before compounding into the paints. In the original drying oils containing no dryers, the quantity required may be as small as 0.05% to 0.2%. In the drying oils alone, the petroleum phenols according to the invention are effective to inhibit the action of gaseous oxygen in containers, and after use, normalize and retard the final stages of oxidation in the film, thus markedly extending the life of the paint or varnish film and increase its strength, flexibility, elasticity and general durability.

The petroleum phenols according to the invention are also effective as gelation inhibitors in tung oil varnish cooking. They do not increase the viscosity of any of the paints, varnishes or enamels in which they are used, and they do not give any false body to such compounds.

In addition the petroleum phenols, especially the redistilled phenols are light in color and have relatively little odor. Accordingly they are not objectionable in the varnish, paint or enamel, and by virtue of their light color they do not darken the varnishes or enamels nor modify the color of paints in which they are used. Furthermore they do not react with dryers such as the naphthenate salts of lead, manganese and cobalt, and other than their anti-skinning and normalizing effect, they are substantially inert and neutral bodies when present in paints, varnishes, enamels, drying oils, etc.

The use of these substances is not limited to the above-described anti-skinning, anti-gelation effects in paints, varnishes, and enamels, but similar advantages are obtained by the use of the petroleum phenols according to the invention in printing inks, divinyl ether and many other oxidizable organic materials. They are efficient as stabilizers of the heavy metal salts of relatively high molecular weight non-aromatic monocarboxylic acids which, generally, have a tendency to decolorize or darken during storage or upon exposure to air. This is especially true of the heavy metal salts of organic acids used as paint and varnish addition agents generally, including dryers, bodying agents, etc. This is especially true of cobalt naphthenate. The addition of small quantities of the petroleum phenols to the cobalt naphthenate, in percentages normally below 2%, preferably between 0.02% and 1% by weight markedly improves the keeping qualities not only of cobalt naphthenate, but other analogous heavy metal salts.

The petroleum phenols may be used as above-described or they may be used in the form of metal salts such as the petroleum phenol salts of zinc, copper, mercury, bismuth, antimony, etc., or as amine salts.

In the above-described example, it was pointed out that the various boiling point cuts of the petroleum phenols were approximately equally efficient and effective, and that mixtures of the several cuts as well as the crude petroleum phenol were also fully and equally effective and efficient.

As above pointed out the redistilled petroleum phenols are light in color, and are particularly adaptable to use in light colored paints and clear varnishes, in which they are free from any tendency to modify or effect the color or clearness. However in the case of heavily colored paints, the crude phenols are fully satisfactory for use in spite of their relatively darker color, since the quantity used is relatively small, and the colored bodies in the crude phenols are of low tinctorial power. The crude phenols may even be used in light colored or even white paints and clear varnishes, at the expense of only a small degradation of color.

The petroleum phenols obtained by extraction from cracked petroleum naphtha made by refinery cracking operations may also be used as above described. The extraction is accomplished by scrubbing with caustic soda solution, which is incidental to the refining of the naphtha for the purpose of correcting color and removing noxious odors. The caustic solution of phenols is then acidified with mineral acids; separated phenolic bodies then rise to the top, and are removed and purified. The resulting products range from 125 to 170 in molecular weight and having boiling points ranging from 215° to 275° C. The lighter cuts comprise principally cresols and xylenols; whereas, the higher boiling cuts contain cresols and xylenols in small proportions, together with large amounts of higher phenolic homologues. The latter fact makes these petroleum phenols an excellent source from which to recover phenolic homologues higher than cresols, which are particularly adaptable to use as anti-skinning agents and oxidation inhibitors in drying oil compositions. Such phenols include homologues ranging from 1-3-4 xylenols to isopseudocuminol. Thus the higher boiling cuts showed much higher efficiency as anti-skinning agents in drying oil compositions than regular commercial grades of phenols or cresols on the market.

By the process and product of the invention, there is thus produced a paint, varnish or enamel composition containing normal varnish, paint and enamel constituents including a drying oil and a dryer, together with a small quantity of petroleum phenol, which by its presence avoids the tendency of paints, varnishes, and enamels to skin in the can, avoids the formation of gel substances either in the can or in the film after application to the surface to be protected, and in addition markedly normalizes and stabilizes the drying action, and avoids erratic and irregular drying in the film, without retarding the drying rate; thereby producing a quick-drying paint, varnish or enamel which keeps well in the can and produces a markedly stronger, tougher, more elastic, more flexible, film when flowed upon the surface to be protected.

While there are above disclosed but a limited number of embodiments of the invention, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed, and it is therefor desired that only such limitations be imposed upon the appended claims as are stated therein or required by the prior art.

The invention claimed is:

1. The method of protecting a drying oil composition against the development of surface skins during storage in the package and improving the toughness, durability and body after application as a protective film on a surface; comprising the steps of incorporating into the drying oil composition a protective substance prepared by distilling out from a petroleum compound a convenient portion of the lower boiling components, thermally cracking the residual higher boiling components and separating from the cracked material a heavy fraction, treating the heavy fraction with strong, aqueous, caustic soda solution, separating purified fuel oil and residual caustic solution from a sodium compound with organic material, acidifying the sodium organic compound solution, and separating a soda-free, oxygen-containing hydrogen and carbon compound therefrom; the said oxygen, carbon and hydrogen compound being combined with the drying oil composition before storage.

2. The method of protecting a paint against the development of surface skins during storage in the package and improving the toughness, durability and body after application as a protective film on a surface; comprising the steps of incorporating into the paint compound a protective substance prepared by distilling out from a petroleum compound a convenient portion of the lower boiling components, thermally cracking the residual higher boiling components and separating from the cracked material a heavy fraction, treating the heavy fraction with strong, aqueous, caustic soda solution, separating purified fuel oil and residual caustic solution from a sodium compound with organic material, acidifying the sodium organic compound solution, and separating a soda-free, oxygen-containing hydrogen and carbon compound therefrom; the said oxygen, carbon and hydrogen compound being combined with the paint substance before storage.

3. The method of protecting a varnish against the development of surface skins during storage in the package and improving the toughness, durability and body after application as a protective film on a surface; comprising the steps of incorporating into the varnish a protective sub-

stance prepared by distilling out from a petroleum compound a convenient portion of the lower boiling components, thermally cracking the residual higher boiling components and separating from the cracked material a heavy fraction, treating the heavy fraction with strong, aqueous, caustic soda solution, separating purified fuel oil and residual caustic solution from a sodium compound with organic material, acidifying the sodium organic compound solution, and separating a soda-free, oxygen-containing hydrogen and carbon compound therefrom; the said oxygen, carbon and hydrogen compound being combined with the varnish before storage.

4. The method of protecting a drying oil composition against the development of surface skins during storage in the package and improving the toughness, durability and body after application as a protective film on a surface; comprising the steps of incorporating into the drying oil composition a protective substance prepared by distilling out from a petroleum compound a convenient portion of the lower boiling components, thermally cracking the residual higher boiling components and separating from the cracked material a heavy fraction, treating the heavy fraction with strong, aqueous, caustic soda solution, separating purified fuel oil and residual caustic solution from a sodium compound with organic material, acidifying the sodium organic compound solution, and separating a soda-free, oxygen-containing hydrogen and carbon compound therefrom; the said oxygen, carbon and hydrogen compound being combined with the drying oil composition before storage in the proportion of 0.1% to 7%.

5. The method of protecting a drying oil composition against the development of surface skins during storage in the package and improving the toughness, durability and body after application as a protective film on a surface; comprising the steps of incorporating into the drying oil composition a protective substance prepared by distilling out from a petroleum compound a convenient portion of the lower boiling components, thermally cracking the residual higher boiling components and separating from the cracked material a heavy fraction, treating the heavy fraction with strong, aqueous, caustic soda solution, separating purified fuel oil and residual caustic solution from a sodium compound with organic material, acidifying the sodium organic compound solution, and separating a soda-free, oxygen-containing hydrogen and carbon compound therefrom; the said oxygen, carbon and hydrogen compound being combined with the drying oil composition before storage together with a dryer comprising a heavy metal naphthenate.

6. The method of protecting a drying oil composition comprising tung oil against the development of surface skins during storage in the package and improving the toughness, durability and body after application as a protective film on a surface; comprising the steps of incorporating into the drying oil composition a protective substance prepared by distilling out from a petroleum compound a convenient portion of the lower boiling components, thermally cracking the residual higher boiling components and separating from the cracked material a heavy fraction, treating the heavy fraction with strong, aqueous, caustic soda solution, separating purified fuel oil and residual caustic solution from a sodium compound with organic material, acidifying the sodium organic compound solution, and separating a soda-free, oxygen-containing hydrogen and carbon compound therefrom; the said oxygen, carbon and hydrogen compound being combined with the drying oil composition before storage.

7. The method of protecting a drying oil composition against the development of surface skins during storage in the package and improving the toughness, durability and body after application as a protective film on a surface; comprising the steps of incorporating into the drying oil composition a protective substance prepared by distilling out from a petroleum compound a convenient portion of the lower boiling components, thermally cracking the residual higher boiling components and separating from the cracked material a heavy fraction, treating the heavy fraction with strong, aqueous, caustic soda solution, separating purified fuel oil and residual caustic solution from a sodium compound with organic material, acidifying the sodium organic compound solution, and separating a soda-free, oxygen-containing hydrogen and carbon compound therefrom; the said oxygen, carbon and hydrogen compound being combined with the drying oil composition before storage together with a thinner, a pigment and a dryer comprising a heavy metal naphthenate.

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