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METHOD OF METAL COATING AND OIL FINISHING COMPOSITION THEREFOR

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This invention relates to metal coating or alloying of metals. More particularly this invention pertains to oleaginous non-aromatic waxy compositions used in tinning, terne coating, lead coating and the like in order to facilitate and aid in coating or alloying a base metal with a uniform and tenacious metal coating.

This process for example, the tinning process comprises essentially coating base metals by dipping and the like said metals into a bath of molten tin thereby coating the base metal with a thin film of metallic tin. The tinning process is carried out at elevated temperatures and when skillfully done with the aid of good fluxing agents and proper tinning oils actually forms an alloy of tin and the metal being treated which is generally iron, steel and other ferrous metals as well as non-ferrous metals such as copper, brass and other alloys.

To insure strong adherence of the tin to the metal surface being coated, the metal must be absolutely clean and free of any grease, dirt, oxide film and rust. This is necessary to insure intimate contact of the metal with the molten tin, terne composition and the like. Metals which are to be coated with tin and the like are therefore carefully prepared by being properly mechanically and chemically treated, pickled and kept in slightly acidic solution in order to prevent oxidation of the metal surface prior to entering the tinning bath or the like.

Briefly stated, for example, one method of tin coating of base metals comprises dipping or passing a properly cleaned metal into a bath of molten tin, on to an oil bath and then through cleaners to remove excess oil and polish the tinned metal surface. The general procedure is to pass a mildly pickled metal plate from a slightly acidified storage tank into a tin pot usually divided into a series of compartments. Each compartment contains a series of rollers through which the metal can pass during its various stages of tin coating. The molten tin occupies the lower or bottom part of the tin pot. On the feed end of the pot floats a layer of flux and on the exit end floats a much deeper layer of oil.

The flux serves to give final preparation of the metal surface before being immersed into the molten tin. It consists generally of zinc chloride or mixtures of zinc chloride and sodium chloride or ferric chloride or ammonium chloride and the like. The function or purpose of the flux is to

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clean thoroughly the metal surface, remove moisture, absorb any oxide film, pickling scum and control more or less the wetability of the metal by the tin so that the molten tin would react and adhere uniformly and tenaciously to the metal surface treated.

From the fluxing bath the metal passes through a series of rollers, through a molten tin bath kept at a temperature of between about 525° F. to above about 800° F. and preferably between about 530°–560°, depending upon the operating conditions. The tinned metal then proceeds through an oil bath while passing through rollers where excess tin is removed, better distribution of the tin coating is secured and oxidation of the tin is retarded. The tinned metal having a thin film of oil on its surface proceeds on out of the oil bath and receives a cleaning treatment where excess oil is removed. Any remaining oil left on the metal aids in polishing the metal to a desired surface finish.

Articles of odd shape can be tin coated by mechanical or hand dipping into a flux coating tin pot and then redipped into an oil covered tin pot which on withdrawal come in contact with the oil and receive its beneficial treatment. If desired the metal can then be immersed into a hot oil bath for final oil treatment in order to more closely control the thickness of the tin coating and also such oil treatment acts to some degree as a quenching medium.

Tinning oils play a vital role in the tinplating art for they serve to secure better distribution of tin on the base metal being coated, aid in removal of excess tin and protect the tin from oxidation or discoloration while being cooled. To accomplish these and other features a good tinning oil must be capable of adsorbing oxides so as to keep the metal surface clean; it must have a suitable interfacial tension with molten tin and with the atmosphere and it must be stable and not tend to deteriorate or polymerize even after long periods of use under extremely high temperatures. Efficient tinning oils should in addition form a uniform film on the coated metal surface while in the tin pot but on emerging from the pot drain off easily and quickly. Oils which do not drain off easily must be continuously replaced which is quite an expense. Such oils also tend to form globules or isolated patches on the tinned surface which produce depressions on the tin

coating, resulting in localities which are very thin and which form grease marks on the tinned surface.

One main criterion of a good tinning oil as stated above is its ability to drain off rapidly from the tinned article as it emerges from the hot oil bath. From this aspect straight mineral oils and even palm oil after relatively short periods of use are not satisfactory. This desirable phenomenon of rapid draining seems to be associated with the presence of certain polar bodies in the oil. An oil containing a plurality of these polar bodies drains off rapidly and leaves the tinned surfaces clean and bright. It is assumed that such oil films tend to form one or more aggregates which move continuously over the surface in an apparently random fashion. As the activity of the aggregates becomes reduced owing to reduction of these polar bodies, the draining rate of the oil is reduced and eventually a "continuous film" state is reached where the draining properties of oils are considerably retarded and the oil is no longer suitable for use. It is postulated that the efficiency of such oils is due to the formation of a monomolecular absorbed oleophobic layer over the surface of the tin.

Generally, oils used in tinplating are subjected to elevated temperatures of at least 460° F. and higher for long intervals. It is therefore essential that such oils be chemically stable at such temperature, without undue volatilization, decomposition or polymerization.

Palm oil is known to be an efficient tinning oil. However, it has several serious drawbacks in that it is costly, difficult to obtain, and above all polymerizes readily at temperatures about 470° F. resulting in sludging and high oil losses. Also beneficial properties of palm oil are destroyed at temperatures above 470° F. since at this temperature it tends to thermally decompose. At this elevated temperature palm oils also tend to leave on the tinplate streaks of oil resulting in a dull, lustreless coated surface.

It is an object of this invention to produce an excellent tinning composition having a non-aromatic hydrocarbon wax-like base. Another object of this invention is to produce a new and improved tinning composition which is stable at extremely high temperatures for long periods of time. Another object of this invention is to produce a new and improved tinning composition having the ability to take up oxide, to readily absorb flux residue and to promote the spreading of tin and other molten metals. Another object of this invention is to produce a tinning composition having excellent draining properties. Still another object of this invention is to produce a tinning composition which does not stain or have bad effects on the coated surface if left on. Furthermore, it is another object of this invention to produce a tinning composition which drains and cleans easily and which is not a fire hazard.

The above and other objects may be attained in accordance with the present invention by admixing with an oleaginous wax-like non-aromatic hydrocarbon a suitable amount of hydrogenated acids obtained from fixed fatty oils, the distillate and residuum fractions of said acids and mixture of said acids and/or their fractions.

Among the hydrogenated animal, vegetable and marine acid products and their fractional derivatives which can be used for metal coating compositions of this invention are:

I. Animal oils
   Tallow (beef, mutton, goat, etc.) oils
   Lard oil
   Bone oil
   Neat's-foot oil
   Wool fat
   Horse foot oil, etc.

II. Vegetable oils
   A. Non-drying oils (hydrogenated)
      Castor oil, cashew nut oil, peanut oil, cocoanut oil, jojoba seed oil, olive oil, olive kernel oil, palm oil, palm kernel oil, etc.
   B. Semi-drying oil (hydrogenated)
      Corn oil, cottonseed oil, kapok oil, rapeseed oil, ravison oil, sesame oil, sunflower oil, teaseed oil, rice bran oil, etc.
   C. Drying oil (hydrogenated)
      Linseed oil, oiticica oil, perilla oil, soybean oil, tung oil, poppyseed oil, hempseed oil, etc.

III. Marine and fish oils (hydrogenated)
   Codfish oil, codliver oil, dogfish oil, dolphin body oil, dolphin fish oil, herring oil, Japfish oil, menhaden oil, porpoise body and jaw oils, salmon oil, sardine and sardine liver oils, seal oil, shark and shark liver oils, sperm whale body and head oils, whale oil, etc.

IV. Hydrogenated residuum fractions obtained from oils listed under Groups I, II, and III.

V. Hydrogenated distillate fractions obtained from oils listed under Groups I, II, and III.

VI. Hydrogenated fatty acids, said fatty acids being prepared by synthetic means e. g.
   A. Oxidation of high molecular weight petroleum hydrocarbons boiling in the range above that of gasoline and to paraffin waxes in accordance with the "Alox Process" of Burwell.
   B. Production of fatty acids by chlorination of paraffin wax, splitting the chlorine by thermal treatment and subjecting the resultant olefines to oxidation treatment in the presence of a catalyst.
   C. Production of fatty acids by the German "Oxo Process" wherein olefines produced by the Fischer-Tropsch process are treated in the following manner:

$$R-CH=CH_2+CO+H_2 \rightarrow RCH_2CH_2CHO$$

   This reaction takes place under 100 to 200 atmospheres pressure and at a temperature of 100 to 200° C. in the presence of a catalyst such as CO—ThO_2—MgO— kieselguhr and the like. The aldehydes thus produced are converted into acids by addition of Na_2CO_3 and air blowing.
   D. Production of high molecular weight fatty acids by the cyanide method in which alkyl halides of high molecular weight are converted into long chain acids through the nitriles.

Hydrogenation of any of the above acids, their distillate and residuum fractions and/or their mixtures can be carried out by any convenient method but preferably under such conditions as in the presence of steam and a suitable catalyst so that the resultant hydrogenated product is acidic. The hydrogenated product should be added to non-aromatic wax-like hydrocarbons in amount sufficient to maintain the acid number of the tinning or metal coating composition at not less than 3 and not above about 15, and pref-

erably between about 4 to 10. In order to maintain the acid number of the composition at approximately these values, a replenishing agent can be added to the wax-like non-aromatic hydrocarbon composition during use. The replenishing agent comprises a concentrate of wax-like hydrocarbons and hydrogenated fatty oil and/or fractions of hydrogenated fatty oils such as the hydrogenated distillate or residuum fractions made up in a ratio varying from 1:3 to about 3:1 parts by weight of each ingredient respectively and preferably the replenishing concentrate is made up of equal parts by weight of wax-like non-aromatic hydrocarbons and the hydrogenated fatty products. The replenishing concentrate is added in amounts sufficient to adjust the acid number of the base composition to not less than about 3 and not above about 15.

Of the hydrogenated fatty acids and their fractions enumerated above, the preferred tin and metal coating oil additives are the hydrogenated fish and/or marine oil distillates and their mixtures. The fish and/or marine oil distillate products can be recovered from such oils by any conventional means and then hydrogenated or the oil can be hydrogenated first and the product then split and the overhead distillate fraction removed by distillation, extraction and the like. For example a fish oil such as herring oil, sardine oil, menhaden oil and the like, can be hydrogenated and split and subsequently distilled to produce an overhead distillate of hydrogenated fish oil. Another preferred fatty oil fraction is obtained by splitting the above hydrogenated fish oil distillate fraction, removing the overhead distillate and utilizing the hydrogenated residuum fraction as the tinning oil additive. The residue product is generally referred to in the trade as fatty acid residuum products or fish oil stearine pitches. The pitch can be further split, subjected to distillation, the overhead distillation fraction recovered, hydrogenated and combined with the first overhead distillate product and used as additive products in this invention. Another method of producing the desired distillate fractions is to split the oil first, remove the distillate fraction and then hydrogenate it preferably in the presence of a suitable catalyst and at elevated temperatures.

The overhead distillate products such as described above or those obtained from other fatty oils are not to be confused with the residue products generally referred to as residuum products or pitches. The two fractions are entirely separate and distinct chemically from each other and also from the base oil from which they are derived. As will be hereinafter shown superior results are obtained when hydrogenated fish oil distillates are utilized as tin and metal coating additives. Under certain tinning conditions an entire hydrogenated fixed fatty oil may be used provided it is stabilized with a suitable antioxidant and/or a draining agent.

Analyses of a hydrogenated marine oil distillate and a hydrogenated marine oil residuum are given below:

Properties	Hydrogenated Marine Oil Distillate	Hydrogenated Marine Oil Residuum
Specific Gravity 60° F	0.950	0.898
Melting Point, °F	145	134
Acid No	188	149
Iodine Value	3.6	23

The non-aromatic waxy base may be waxy hydrocarbons derived from petroleum fractions such as petroleum distillates or residues, or the waxy hydrocarbons may be produced synthetically by polymerization of olefinic material by the Fischer-Tropsch process or by dehydration of long chain aliphatic alcohols, said waxy non-aromatic hydrocarbon thus produced having a minimum flash point of about 500° F. and preferably higher, or they may be produced by any other suitable means.

Waxy hydrocarbons such as the non-aromatic or non-ring waxy hydrocarbons may be recovered from suitable petroleum fractions such as Pennsylvania crudes, East Texas crudes, Mid-Continent crudes and the like by de-asphaltizing the hydrocarbon and thereafter removing the wax from the asphalt free hydrocarbon fraction by any known suitable means. The asphalt may be separated from the oil either by distillation or solvent extraction, although solvent extraction is preferred. In this process a solvent is selected in which the oil is relatively soluble but in which the asphaltic materials are relatively insoluble. Among such solvents are the light liquid hydrocarbons such as ethane, propane, butane, as well as naphtha and gasoline. Oils treated with such solvents extract the oil and wax leaving behind the asphaltic materials as residue. The wax-oil mixture may be removed from the asphalt-free solution by chilling the solution, and then separating the precipitated wax by settling, filtering or centrifuging. Waxy materials thus produced are known in the art as slop waxes, petrolatum stock, slack waxes, scale waxes, paraffin waxes, plate, malcrystalline and needle waxes, micro-crystalline waxes and the like. These waxes are differentiated from each other by the degree of de-oiling to which they are subjected and all of them may be used as bases of compositions of this invention provided they are substantially free from aromatics.

De-waxing or separation of the above waxy constitutents from the oil may be accomplished by selective solvent treatment using as the diluents liquefied normally gaseous hydrocarbons such as propane, butane and other corresponding olefins and/or their mixtures as well as oxygen-containing liquid organic substances such as alcohols, ethers, esters, ketones, aldehydes, acids and/or their mixture. These may include, methyl, ethyl, propyl, butyl, amyl alcohols; methyl or ethyl or methyl ethyl ether; acetones, diethyl, dimethyl, methyl ethyl, methyl isobutyl ketones and the like. Chlorinated hydrocarbons such as carbon tetrachloride or trichloroethylene and mixtures of chlorinated and non-chlorinated hydrocarbons as mentioned above also may be used.

The first step in obtaining waxy constituents from petroleum crudes for example such as Mid-Continent crude is to treat said crude with about six volumes of liquid propane so as to remove the asphalt. The propane from the propane-oil solution is vaporized so that the ratio of propane to oil is reduced approximately 2 to 1. The solution is then chilled to about —40° F. and lower causing separation of the wax from the oil. The wax can be removed by filtration and the propane separated from the de-asphalted and dewaxed oil and waxy material by distillation. A most desirable wax friction may also be obtained from Pennsylvania waxy steam cylinder stock by treating a waxy portion of said

stock with methyl ethyl ketone so as to obtain two fractions, one being dewaxed oil and the other fraction being what is known as whole wax. This whole wax is also treated with methyl ethyl ketone from which again two separate fractions are obtained, one fraction being partially deoiled microcrystalline residue wax which contains about 5 to 6% oil and has a melting point of about 130° F. and the other fraction being the so-called slop wax or foot's oil, having a melting point of about 65°. This so-called slop wax is particularly suitable as a base for compositions of this invention.

Waxy materials can also be recovered from distillate or residuum lube oil fractions and these wax fractions can be split still further into special wax cuts having desired characteristics by use of selective solvents. This is based on a difference in solubility of different waxy fractions in a given solvent. Thus when using a methyl ethyl ketone type solvent the aromatic constituents can be removed by successive cooling the mixture down to between about −40 to −60° C. so as to remove the aromatics which become substantially soluble in the solvent as the temperature is lowered while the straight chain waxes and isoparaffins become substantially insoluble in the solvent. The straight chain waxes can be separated from the isoparaffins by extraction and fractional crystallization. Depending upon the distillate cut used waxes of from 12 to above 36 carbon atoms and higher can be obtained.

Instead of obtaining natural paraffinic waxes from petroleum fractions in the manner indicated above, straight chain waxes can be produced synthetically by polymerization of olefins under pressure or dehydrating long chain fatty alcohols such as octadecyl alcohol and the like. This non-ring containing waxy product can be prepared by catalytically dehydrating octadecyl alcohol at between about 375 to 450° F. to yield mixtures of monomers and dimers of C_{18} olefins and C_{36} olefins, respectively. If desired these fractions can be separated by atmospheric steam distillation at 550–590° F. and moisture can be removed by any suitable means.

The above non-aromatic waxy materials may be used as the sole carrier for the hydrogenated fixed fatty acids or admixed with minor amounts of other types of natural and synthetic waxes or chemical derivatives thereof so as to improve the draining and tinning properties of compositions of this invention. Among such products may be mentioned, oxidized paraffin wax, wool fat, lanoline, beeswax, insect wax, montan wax, and the like. Substantially any natural or synthetic waxy non-aromatic containing material or mixtures thereof can be used as the base for compositions of this invention.

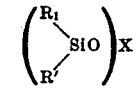
If desired anti-oxidants may be added to compositions of this invention in order to stabilize it during use. Anti-oxidants which are particularly preferred are the high boiling nitrogen containing organic compounds such as high boiling point aromatic amines.

Among the amine compounds which can be included for use in this invention are the aromatic amines, aliphatic amines, alkylarylamines, cyclic amines, heterocyclic amines and the like and their mixtures. The following amine compounds are applicable as stabilizing agents for metal coating compositions of this invention: paraphenylene diamine, alpha-naphthylamine, orthophenylene diamine, beta-naphthylamine, 5-dibeta-naphthyl para phenylene diamine, 2,4-diamino diphenylamine, meta toluylene diamine, 2-amino-1,4-naphthohydroquinone, 4-amino - 1,2 - naphthohydroquinone, thiodiphenylamine, monobenzyl para amino phenyl, 2,4-diamino toluene, 2,4-diamino diphenyl amine, para amino azobenzene, octadecyl benzyl amine, beta phenylamine-alpha-naphthylamine, phenyl - α - naphthylamine, phenyl - β - naphthylamine, N,N'dibutyl para phenylene diamine, tetra methyl diamino diphenyl methane, p,p'-diamino diphenyl methane, 4,4-diamino diphenyl methane, tetraethyl diamino diphenyl methane, diisoamyl diamino diphenyl methane, bis-β-naphthyl amino methyl)-p-tertamyl phenol; 3,3,5 tricyclohexylamine, dicyclohexylamine; N-phenyl morpholine, N-(parahydroxy-phenyl) morpholine; octadecyl 3-methyl-2-pentylamine, N-octadecyl-2-ethylhexylamine, hexadecylamine, octadecylamine, octadenylamine, octadecadienyl amine, paraffin wax amine, cocoamine prepared from cocoanut oil acids, N,N'-dimethyl triglycol diamine; disalicylal ethylene diamine; N-salicylal-N'-ethanolethylene diamine; 5 methyl,2,4-diamino anisole; ketone diarylamine, ketone amine; ketone amine condensation products; butyraldehyde aniline derivatives; condensation products of acetone and aniline, reaction products of acetone and para amino diphenyl. In addition to the above amine compounds the following mixtures of amines produce good stabilizers. Mixtures of diphenyl paraphenylene diamine and isopropoxydiphenylamine, phenyl - α - naphthylamine and meta toluylene diamine, mixture of dipara methoxy diphenyl amine, diphenyl para-phenylene diamine and phenyl beta naphthyl amine, mixtures of phenyl β naphthylamine and meta toluylene diamine, mixture of diphenyl para phenylene diamine and para phenylene diamine, mixture of stearic acid, meta toluylene diamine and phenyl - α - naphthylamine, mixture of ditolylamine and petroleum wax and the like. The amines which are particularly preferred are: phenyl-α-naphthylamine, phenyl-β-naphthylamine, beta phenylamine-alpha-naphthylamine, tetra methyl diamino diphenyl methane, meta toluylene diamine, their mixtures and amines having a boiling point of or above that of phenyl-α-naphthylamine, although this is not a critical limitation but a desirable one.

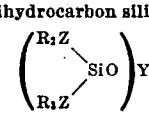
The addition of nitrogen-containing organic compounds to compositions of this invention in addition to inhibiting the oxidation tendencies of the composition greatly improves its tinning properties and stability. In addition it reduces the rate of viscosity increase due to oxidation and improves the draining of the composition from the tin plate.

Compounds which possess the property of aiding draining of the tinning compositions of this invention also may be added and these include the broad class of oxygen containing polar organic compounds having oleophilic substituent groups. Among such compounds are:

A. Organic silicone compounds of the following classes:



dihydrocarbon silicone



dihydrocarbon silicate

in which R_1, R_2 and R_3 are hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, alkaryl radicals, preferably having a total of not more than about 20 carbon atoms; R' is a hydrogen or a hydrocarbon radical; Z and Z are oxygen, sulfur, selenium or tellurium atoms; and X and y are positive integers preferably 2 or higher. With regard to y it is believed that it should preferably be not higher than about 6. The first formula may be illustrated by dimethyl silicone:

$$[(CH_3)_2SiO]_x$$

The second formula is illustrated by di-ethyl silicate:

$$[(C_2H_5O)_2SiO]_y$$

The two R's and the two Z's of the above formulae may be identical or different in each monomer and such monomeric units may be polymerized with identical or different monomeric units. Among the many radicals represented by the several R's especial reference may be made to methyl ethyl, normal and isopropyl; normal, iso, secondary and tertiary butyl; various amyl, hexyl, heptyl, octyl and homologous groups. Also of value are such radicals as cyclopentyl, cyclohexyl, phenyl, benzyl, tolyl, naphthyl and the like.

B. Oxidized hydrocarbons
Refined oxidized paraffin wax

C. Organic condensation reaction products of:
1. Octadecylene and maleic anhydride (iodine catalyst)
2. Steam distillate from the product of condensation of octadecene obtained by dehydration of n-octadecanol with maleic anhydride
3. Long chain olefin with maleic anhydride
4. Long chain olefin with maleic anhydride and an alcohol
5. Long chain olefin with maleic anhydride and a base with or without an alcohol
6. Long chain olefin with maleic anhydride and an organic acid such as oleic acid
7. Abietic acid (rosin acids) with maleic anhydride and stenol and the like
8. Acetone in caustic solution under elevated temperature and pressure to produce high molecular weight unsaturated ketones having at least 12 and preferably more than 18 carbon atoms in the molecule
9. Alkyl phenol with an aliphatic aldehyde (formaldehyde) said product thereafter or during condensation being treated with a metal preferably an alkaline earth metal and the like.

D. Organic acids
Sulfurized oleic acid and the like
Abietic acid and the like

E. Phosphate derivatives
Dilorol phosphate
Triphenyl phosphate
Diisoamyl potassium pyrophosphate
Pentacapryl stearylamine tripolyphosphate
Triethylamine tetrapolyphosphate
Mono oleyl dipolyglycol ortho phosphate
Pentabutyl tripolyphosphate
Dibutyl ammonium pyro phosphate
Tetrabutyl phosphate
Triethyl ammonium tetra polyphosphate
Mono-oleyl dipoly glycol ortho phosphate

F. Amides
tri(dibutylamine) phosphamide and the like

G. Salts of organic compounds
Na oleate
Ca phenyl stearate
Salts of rosin acids
Zn salts of diisopropyl salicylate and the like
Ca cetyl phosphate and Ca cetyl phenate mixture

The oxygen containing polar organic draining agents which are particularly preferred are: silicones, abietic acid, diisopropyl salicylate, Zn salt of diisopropyl salicylate, Ca salt of alkyl phenol-formaldehyde condensation reaction product, rosin soap, diisoamyl potassium pyrophosphate and triethyl ammonium phosphate.

To more fully and clearly illustrate this invention a series of comparative tinning tests were conducted in which the tinning performance as to flux removal, drainage characteristic, ease of cleaning and spreadability characteristics of the following compositions were compared:

Code No.
1. Mineral oil (solvent extracted Mid-Continent oil, 150–170 SUS at 212° F.)
2. Palm oil.
3. 20–50% by weight of palm oil in mineral oil base.
4. Mixture of hydrogenated cottonseed oil in mineral oil base having an acid number of less than 3.
5. Mixture of hydrogenated fish oil residuum or stearine pitches in mineral oil having an acid number of 3 to 15.
6. Mixture of hydrogenated fish oil residuum or stearine pitches in mineral oil having an acid number of 3 to 15 and containing about 0.5% by weight of phenyl-α-naphthylamine.
7. Mineral of hydrogenated fish oil distillates in mineral oil having an acid number of 3 to 15.
8. Mixture of non-aromatic waxy material of the group of petroleum fraction comprising petrolatum, slop wax and slack wax and a hydrogenated fish oil residuum or stearine pitches having an acid number of 3 to 15.
9. Mixture of non-aromatic waxy material of the group of petroleum fraction and comprising petrolatum, slop wax and slack wax and hydrogenated fish oil distillates having an acid number of 3 to 15.
10. Pennsylvania cylinder stock slop wax containing hydrogenated fish oil distillates in amounts sufficient to maintain the acid number of the composition at between about 3 to 15.
11. C_{36} liquid dimer obtained by dehydrating long chain fatty alcohols containing hydrogenated fish oil distillates in amounts sufficient to maintain the acid number of the composition at between about 3 to 15.
12. Pennsylvania cylinder stock slop wax containing hydrogenated fish oil distillates in amounts sufficient to maintain the acid number of the composition at between about 3 to 15 and 0.5 to 1% phenyl-α-naphthylamine.

One test was conducted as follows:

A. Pickled sheets of black plate, stored in 0.5 per cent HCl, were dipped in flux (3 pounds $ZnCl_2$ plus 5 ounces NH_4Cl per gallon) and tinned at temperatures between about 530–560° F., and preferably at 550° F. The tinning pot surface was covered with flux. Sheets were tinned so that very little, if any, flux adhered to the sheets

upon withdrawal. Immediately after withdrawal, the sheets were transferred to a finishing pot containing tin at 530–545° F. and a superimposed layer of oil at 460–490° F. and preferably at 470° F. The relatively high tin pot temperature was necessary in order to maintain the tin in a desired third state for tinning. Here the metal sheets were immersed in the tin and then drained in the oil layer. Metal strips tested were given a tinnning and oil treatment at regular intervals, and the test was conducted for a period of 72 hours. The properties as indicated in Table I were graded in descending order, (0) being the best, (1) next best, etc. The results of the test were as follows:

into the bottom of the wax pot. Tests were conducted for a 72 hour period with the same compositions as indicated in Table I and the results were substantially the same as indicated in Table I.

C. Still another test was conducted in a small tinning machine similar to that described in columns 1 and 2. The tin was melted, put in the wax containing pot and the flux and wax composition tested put in the feed end or exit compartments of the machine respectively. The temperature of the wax composition was kept in the range of 475°–490° F. Approximately three tests with each composition were conducted during a 24 hour interval and the tinning perform-

TABLE I

Code No.	Flux Removal	Draining Characteristics	Ease of Cleaning	Spreading Characteristics	Total	Remarks
1	10. Poor flux removal.	10. Streaked badly.	10. Flux spots, stained, sticky.	10. Stained, stripped, heavy tinned.	40	Mineral alone was found totally unsuitable. At the end of 24 hrs. sludge formations were high and losses heavy so that test had to be discontinued.
2	3. Showed good flux removal for 72 hr. test.	5. Good draining characteristics for early part of test but streaked after 48 hours.	4. Easy but flux spots noted.	3. Good at early stage but spangled after 24 hrs.	15	Although the tinning characteristics of of palm oil were good for 24 hours oil losses were heavy at the end of the 72 hour test.
3 30% Palm oil in mineral oil.	6	8. Poor throughout test period.	8. Easy to remove but flux spots noted.	7. Stained	29	After 24 hours the tin plate was stained and spangled. Stripping was noted and draining was poor throughout test. At the end of 24 hours test was discontinued.
4	6	10. Streaked badly	8. Stained and difficult to clean.	10. Stained, tinning not very uniform.	34	After a short period the oil was found to be unsatisfactory and test was discontinued.
5	3	8. Poor throughout test period.	8. Good draining early period of test but became worse later.	4. Fair	21	Flux removal and spreading were good. Draining and cleaning were poor and became increasingly worse.
6	3. Good flux removal for 72 hours.	5. Good draining at first but became worse as test continued.	3. Good	3. Good at beginning of test but left stains.	14	The addition of the amine antioxidant resulted in a product equivalent to or superior to palm oil.
7	1. Good	3. Good for 48 hours, but at end of test period showed signs of poor draining.	3. Same	2. Good	10	Flux removal and spreading were good. Exhibited a pronounced stabilizing effect on the composition and gave good tinning performance at the end of 72 hrs. Oil losses were only ¼ of that of palm oil after 72 hrs.
8	1. Very good	2. Good for entire 72 hour test.	2. Good	2. Good	7	This composition gave excellent tinning performance for entire test period. Flux removal and spreading were good. Exhibited good tinning performance for entire 72 hr. test period. Losses were much lower at least ¼ lower than were experienced when palm oil was used and also less replenishing agent was required in order to maintain the acid number of the composition at between 3 to 15.
9	0. Very good	0	0	0	0	Do.
10	0	0	0	0	0	Do.
11	0	0	0	0	0	Do.
12	0	0	0	0	0	This composition gave excellent tinning performance for over 72 hours. Required substantially no replenishing agent and exhibited excellent spreading and drawing properties.

B. Another test was conducted in which the tinning technic was slightly modified. Two tinning pots were used as before, and the temperature of the first tin pot was kept at 535° F. and the final pot at 475° F. Instead of the waxy layer on the second pot, a small amount of tallow just sufficient to form a ring covering the bath edges was used to keep the surface clean. Immediately upon withdrawal of the sheet from the second pot, it was transferred to a wax pot kept at a temperature of 460–475° F. To simulate the wax-tin interface encountered in tinplate manufacture, a small amount of tin was poured into the bottom of the wax pot. Tests were conducted for a 72 hour period with the same compositions as indicated in Table I and the results were substantially the same as indicated in Table I.

ance of the composition as to flux removal, draining characteristics, ease of cleaning and spreading characteristics were noted. The results again were similar to those disclosed in Table I, showing the superiority of tinning composition of this invention and particularly tinning composition containing a hydrogenated fish oil distillate.

D. Tests were conducted according to procedure outlined under A and B in order to determine the criticality of maintaining the acid number of non-aromatic waxy material-hydrogenated fatty oil products and their fractions between about 3 to 15.

TABLE II

		Flux Removal	Draining Characteristics	Ease of Cleaning	Spreading Characteristics	Total	Remarks
1	Mixture of non-aromatic waxy material extracted from a petroleum fraction comprising petrolatum, slop wax and slack wax and hydrogenated fish oil distillates having an acid number less than 3.	8	9	7	6	30	Drained very poorly and unstable.
2	Mixture of non-aromatic waxy material extracted from a petroleum fraction comprising petrolatum, slop wax and slack wax and hydrogenated fish oil distillates having an acid number greater than 15.	3	6	7	4	20	Cause etching of metal surface and difficult to clean.
3	Mixture of non-aromatic waxy material extracted from a petroleum fraction comprising petrolatum, slop wax and slack wax and hydrogenated fish oil distillates having an acid number between about 4–10.	0	0	0	0	0	Excellent tinning results during entire test time.

A quick and indicative test was developed to study the draining characteristics of wax-like oleaginous tinning compositions. A heavily tinned plate was immersed for 15 seconds into a tinning composition kept at a temperature of approximately 480° F. Heavily tinned plates were dipped in the various oleaginous compositions at intervals during a 48 hour interval, the draining characteristics were observed on the test plates after the removal from the bath, and the characteristics of the oleaginous film remaining on the plate were preserved by printing off on a hard filter paper while still somewhat warm.

TABLE III

	Composition	
1	Mineral Oil	Drained poorly through test period. Filter paper covered with a heavy oil film.
2	30% by wt. of Palm oil in mineral oil.	Drained poorly, paper covered with an oil film.
3	Mineral oil-hydrogenated fish oil distillates having an acid number less than 3.	Do.
4	Palm Oil	Drained very well, few oil spots on paper.
5	Mineral oil-hydrogenated fish oil distillates having an acid number between 3 and 15.	Equal to, if not superior to, palm oil in draining characteristics.
6	Mineral oil-hydrogenated cottonseed oil having an acid number of less than 3.	Drained very poorly during test peri
7	Pennsylvania Cylinder Stock Slop wax-hydrogenated fish oil distillates having an acid number between 3 and 15.	Excellent tinning results.
8	C_{36} liquid dimer-hydrogenated fish oil distillates having an acid number between 3 and 15.	Do.

Compositions of this invention are not restricted to use in tinplating only but are equally applicable for terne coating, lead coating and the like. Neither are these compositions restricted to use where metal plating is done only by dipping and the like. Compositions of this invention can be used to improve the metal coating surface and deposition of metals on metal base by electrolytic methods as well as any other known metal plating method. The appearance of surfaces having tin deposited thereon by electrolytic means is greatly improved by dipping such metal treated surfaces into a hot bath comprising an oleaginous composition of this invention.

In addition to being equal to and in most properties superior to palm oil, compositions of this invention have a particular advantage over palm oil in that they reduce to a minimum the danger of fire hazard.

It is to be understood that while the features of the invention have been described and illustrated in connection with specific compositions, the invention is not limited thereto or otherwise restricted, except by the prior art and the scope of the appended claims.

I claim as my invention:

1. A composition suitable for aiding in forming an adherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of slop wax free from aromatics and partially hydrogenated fish oil distillates said mixture having an acid number of from about 4 to 10 and a minor amount sufficient to stabilize the composition against deterioration of phenyl-α-naphthylamine.

2. A composition suitable for aiding in forming an aherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of a polymeric olefin obtained by dehydrogenation of long chain aliphatic alcohols free from aromatics and partially hydrogenated fish oil distillates said mixture having an acid number of from about 4 to 10 and a minor amount sufficient to stabilize the composition against deterioration of phenyl-α-naphthylamine.

3. A composition suitable for aiding in forming an adherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of Mid-Continent residual petrolatum free from aromatics and partially hydrogenated fish oil distillates said mixture having an acid number of from about 4 to 10 and a minor amount sufficient to stabilize the composition against deterioration of phenyl-α-naphthylamine.

4. A composition suitable for aiding the formation of an adherent tin coating on ferrous surfaces, consisting essentially of a mixture of a waxy hydrocarbon free from aromatics and partially hydrogenated fish oil distillates said mixture having an acid number of from about 4 to 10 and a minor amount sufficient to stabilize the composition against deterioration of phenyl-α-naphthylamine.

5. A composition suitable for aiding in forming an adherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of waxy hydrocarbons free from aromatics and a hydrogenated fish oil residue and said mixture having an acid number of from about 4 to 10 and a minor amount sufficient to stabilize the composition against deterioration of phenyl-α-naphthylamine.

6. A composition suitable for aiding in forming an adherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of a waxy hydrocarbon free from aromatics and a hy-

drogenated fixed fatty oil distillate said mixture having an acid number of from about 3 to 15.

7. A composition suitable for aiding in forming an adherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of a waxy hydrocarbon free from aromatics and a hydrogenated fixed fatty oil said mixture having an acid number of from about 3 to 15.

8. A composition suitable for aiding in forming an adherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of a waxy hydrocarbon free from aromatics and a hydrogenated fixed fatty oil said mixture having an acid number of from about 3 to 15 and a minor amount sufficient to stabilize the composition against deterioration of an aromatic amine.

9. A composition suitable for aiding in forming an adherent smooth tin coating on ferrous surfaces, consisting essentially of a mixture of a non-aromatic waxy hydrocarbon and a hydrogenated fish oil distillate said mixture having an acid number of from about 4 to 10 and minor amounts of phenyl-alpha-naphthylamine, and a minor amount sufficient to aid draining, of dimethyl silicone polymer.

10. In a method of metal coating of metal surfaces, wherein said metal surfaces are first cleaned and pickled and wherein said cleaned metal is passed successively first through a molten flux bath, then through a molten bath of a metal selected from the class consisting of molten tin, molten lead and a mixture of lead and tin and then passing said treated metal through an oleaginous waxy composition maintained at an elevated temperature, the improvement which comprises using as said oleaginous waxy composition a mixture consisting essentially of slop wax and hydrogenated fish oil distillate, said mixture having an acid number of from 4 to 10, a minor amount sufficient to stabilize the composition against deterioration of phenyl-α-naphthylamine and a minor amount, sufficient to aid draining of dimethyl silicone.

11. In a method of metal coating of metal surfaces, wherein said metal surfaces are first cleaned and pickled and wherein said cleaned metal is passed successively first through a molten flux bath, then through a molten bath of a metal selected from the class consisting of molten tin, molten lead and a mixture of lead and tin and then passing said treated metal through an oleaginous waxy composition maintained at an elevated temperature, the improvement which comprises using as said oleaginous waxy composition a mixture consisting essentially of slop wax and hydrogenated fish oil distillate, said mixture having an acid number of from 4 to 10, a minor amount sufficient to stabilize the composition against deterioration of phenyl-α-naphthylamine.

12. In a method of metal coating of metal surfaces, wherein said metal surfaces are first cleaned and pickled and wherein said cleaned metal is passed successively first through a molten flux bath, then through a molten bath of a metal selected from the class consisting of molten tin, molten lead and a mixture of lead and tin and then passing said treated metal through an oleaginous waxy composition maintained at an elevated temperature, the improvement which comprises using as said oleaginous waxy composition a mixture consisting essentially of a waxy hydrocarbon free from aromatics and a hydrogenated fixed fatty oil, said mixture having an acid number of from 3 to 15 and a minor amount, sufficient to stabilize the composition against deterioration of an aromatic amine.

13. In a method of metal coating of metal surfaces, wherein said metal surfaces are first cleaned and pickled and wherein said cleaned metal is passed successively first through a molten flux bath, then through a molten bath of a metal selected from the class consisting of molten tin, molten lead and a mixture of lead and tin and then passing said treated metal through an oleaginous waxy composition maintained at an elevated temperature, the improvement which comprises using as said oleaginous waxy composition a mixture consisting essentially of a waxy hydrocarbon free from aromatics and a hydrogenated fixed fatty oil, said mixture having an acid number of from 3 to 15.

14. A composition suitable for aiding in forming an adherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of waxy hydrocarbon free from aromatics and a hydrogenated fixed fatty oil residue, said mixture having an acid number of from about 3 to 15.

15. A composition suitable for aiding in forming an adherent and smooth tin coating on ferrous surfaces, consisting essentially of a mixture of slop wax free from aromatics and hydrogenated fish oil distillates, said mixture having an acid number of from about 4 to 10 and a minor amount sufficient to stabilize the composition against deterioration of phenyl-alpha-naphthylamine.

16. In a method of metal coating of metal surfaces, wherein said metal surfaces are first cleaned and pickled and wherein said cleaned metal is passed successively first through a molten flux bath, then through a molten tin bath and then passing said treated metal through an oleaginous waxy composition maintained at an elevated temperature, the improvement which comprises using as said oleaginous waxy composition a mixture consisting essentially of slop wax and hydrogenated fish oil distillate, said mixture having an acid number of from 4 to 10 and a minor amount sufficient to stabilize the composition against deterioration of phenyl-alpha-naphthylamine.

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