ABSTRACT OF THE DISCLOSURE

Single package "C" enamel produced by blending a base of a hydrocarbon resin modified with drying oils, preferably linseed and tung oils, in combination with a zinc paste made by grinding zinc oxide into a maleic anhydride-dimerized resin product modified with linseed, dehydrated castor oil and/or tung oil acids wherein excess acid groups have been neutralized with a polyhydric alcohol. The "C" enamel may contain 1 to 45% by weight, and preferably from 1 to 25% by weight, of pure zinc oxide and is a stable, non-reactive product which can be held in storage containers for periods of up to one year without excessive viscosity increases and with virtually no settling of the zinc oxide.

The present invention relates to an improved "C" enamel, and more specifically relates to a single package "C" enamel of outstanding stability.

BACKGROUND OF THE INVENTION

For many years an oleo-resinous varnish known to the trade as "C" enamel has been used to coat the interior of vegetable cans and other cans designed to contain wet foodstuffs. This "C" enamel contains zinc oxide, which gives a partially opaque or milky appearance to the coating and reduces the formation in the container of iron sulfides, which cause a blackening of the container and the canned product. It is believed that a preferential reaction takes place between the zinc oxide and the sulfur compounds in the food to produce zinc sulfide, which, like zinc oxide, is white. If the zinc oxide is not present in the can coating, sulfide compounds in the foods will react with the ferrous container and produce a black, insoluble iron sulfide. While iron sulfide is not particularly toxic or harmful, it does affect the taste and the color of the food inside the container, and especially imparts a very unappetizing appearance to the food. The zinc sulfides which are formed by the preferential reaction of sulfur compounds with zinc oxide are colorless and are not detrimental to the container or product in either appearance or taste.

Prior to the present invention, "C" enamels have always been prepared in the form of two separate components, namely, coating enamel and a zinc paste (an enamel pigmented with zinc oxide). These two components are kept separate and are only blended together shortly before the application of the resulting "C" enamel to the container. This separated packaging with blending immediately prior to use is required due to the rapid viscosity increase in the blended "C" enamel. More particularly, the viscosity increase is of such a magnitude that after a few hours standing the blend becomes too thick to be usable.

This effect is believed due to the highly reactive nature of the zinc oxide. The most stable of the "C" enamel can coatings of the prior art demonstrate a shelf stability of about 1½ hrs. when blended with the zinc oxide.

OBJECTS OF THE INVENTION

It is an object of this invention to provide an improved single package "C" enamel with greatly increased storage stability.

It is an additional object of this invention to provide a single package coating "C" enamel containing 1 to 45% by weight of zinc oxide with a shelf stability of at least 6 months. It is another object of this invention to provide a process for the production of a single package "C" enamel containing 1 to 45% by weight of zinc oxide with greatly improved shelf stability.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes or modifications within the scope of the invention will become apparent to those skilled in the art from this detailed description.

DESCRIPTION OF THE INVENTION

The improved single package "C" enamel of the present invention is produced by blending a base of a hydrocarbon resin modified with drying oils, preferably linseed and tung oils, in combination with a zinc paste made by grinding zinc oxide into a maleic anhydride-dimerized resin product modified with linseed and dehydrated castor oils or acids wherein excess acid groups have been neutralized with polyhydric alcohols. The blended "C" enamel may contain 1 to 45% by weight, and preferably from 1 to 25% by weight, of pure zinc oxide and is a stable, non-reactive product which can be held in storage containers for periods of up to one year without excessive viscosity increases and with virtually no settling of the zinc oxide. This ready mixed, or single-package, "C" enamel may be applied to metal substrates by a variety of methods, such as roller coating, spraying, curtain or flow coating, etc., and may be baked at temperatures of, for example, 350° to 600° F.

The present storage-stable single package "C" enamels of this invention are achieved by the use of particular petroleum hydrocarbon bases. It is essential that the petroleum hydrocarbon base be essentially free of acid groups. The preferred petroleum hydrocarbon base is a product sold under the trade name "Neville L-X-782," which is a neutral, unsaponifiable resin (that is, it is not an acid or an ester), which has a ball and ring method softening point of 102° C., an iodine number of 160, and a Gardner-Holdt viscosity at a concentration of 70 per cent solids in Varsol of Z-9. Any petroleum hydrocarbon resins which are fairly high in unsaturation and which do not contain an appreciable amount of acid or ester groups may be used as the base of the "C" enamel of this invention. For example, still-bottom residues, produced after petroleum cracking operations, which have a softening range of 80-125° C., and are fairly high in unsaturation, may be used as the petroleum hydrocarbon base. Other commercially available petroleum hydrocar-
bon resins which may be utilized besides Neville L-X-782 are various other Neville products and the resin sold under the trade name "Velsicol."

Any of the conventional drying oils which have been utilized by the paint and varnish industry may be used to modify the petroleum hydrocarbon base. Preferred drying oils are linseed oil, dehydrated castor oil, fish oil and tung oil. Mixtures of several drying oils may be used if desired.

Generally, 50 to 60 percent by weight of drying oil and 40-50 percent by weight petroleum hydrocarbon resin, will be used to prepare the varnish base.

The term "petroleum hydrocarbon resin" in the present specification and claims is to be construed broadly as any resinous petroleum hydrocarbon product which contains a fairly high degree of unsaturation and has a saponification number of less than .5 and an acid number of less than .5.

The varnish is prepared by heating the petroleum hydrocarbon varnish resin and the tung oil, linseed oil or other drying oil at a temperature of 260 to 290° C, preferably at a temperature of 275 to 280° C, for the period of time necessary for the varnish to reach the desired viscosity. Generally, the desired viscosity will be of G to K (Gardner scale) and is preferably approximately "J" on the Gardner scale when reduced to 50% non-volatile in mineral spirits. The varnish so produced is a clear solution.

The zinc paste varnish is a maleic anhydride-dimerized rosin hard gum, modified with linseed, tung, or dehydrated castor oil acids or mixtures thereof, which are preferably neutralized with glycerine or pentaerythritol, although any polyhydric alcohol can be used to neutralize the excess free acid groups. While dimerized resin is preferred, resin may be used as a substitute therefor. Suitable resin acids which may be used, which, however, are not as effective as dimerized resin, include, for example: abietic acid, levopimaric acid, neoabietic acid, dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid, dextropimaric acid, and isodextropimaric acid.

If desired, fumaric acid may be substituted for the maleic anhydride.

The dimerized resin is believed to consist of about 10% non-acid material and about 90% of dimerized acids which are believed to have the following structural formula:

These dimerized resin acids may be further characterized by their saponification values. The dimerized resin acids used in the present invention preferably have a saponification number of from about 140 to about 160. These dimers are readily available as commercial products.

The zinc paste varnish is prepared by heating the dimerized resin, the maleic anhydride, the linseed or dehydrated castor oil acids, and the glycerol or pentaerythritol together at a temperature of 250 to 290° C, and preferably about 275° C, until a viscosity of G-I (Gardner scale) when reduced to 50% non-volatile in mineral spirits is obtained, at which time the acid number should be no greater than 15.

The maleic anhydride, dimerized resin, and linseed or castor oil acids are believed to form a condensation product through unsaturated reactive sites, although the present invention is not to be limited to any particular theory of reaction type or mechanism. For example, the conden-

sation of maleic anhydride with levopimaric acid is known to proceed by the following equation:

The zinc paste is produced by dispersing pure zinc oxide, for example, by sand milling, roller milling, pebble milling, etc., into the zinc paste varnish at concentrations of 30% up to 80% by weight of zinc oxide based on the weight of the grinding vehicle. The zinc oxide should be essentially water-free. The zinc oxide paste may be produced at room temperature or at elevated temperatures as desired. The paste usually heats up during the process, and therefore, the dispersed product is usually obtained above room temperature. While the amount of the zinc oxide may be varied over cited ranges, obviously the most economical concentration which will be sufficient to control the sulphur compounds in the foods will be utilized. Generally, the composition of the zinc paste varnish will be the following, wherein the ranges are of percent by weight: maleic anhydride 5 to 20; dimerized resin 24 to 44; drying oil acids 45 to 56; and polyhydric alcohol 4.1 to 10.

The proportion of zinc oxide to zinc paste varnish in the zinc paste will vary from 30 to 80% by weight and the zinc oxide in the "C" enamel may vary from 1 to 45% by weight, preferably 1 to 25% by weight. Generally, about 5 to about 50% by weight of the zinc paste, based on total weight, will be mixed in the varnish base.

Conventional adjuvants may be added to the single package "C" enamel of this invention, i.e., conventional driers and lubricants may be added to the "C" enamel of this invention without reducing the storage stability of the composition.

While the improved single package "C" enamel of this invention was primarily intended for coating flat stock which is to be converted into cans for containing wet foodstuffs, the application of the present invention in other coating applications wherein zinc oxide is utilized will be readily apparent to one of ordinary skill in the art. The enamels of the present invention are as good as the conventional two-package enamels previously produced as far as process and chemical resistance characteristics are concerned, but offer the decided advantage of a single-package system with a shelf stability of up to one year without an increase in viscosity.

The invention will be more clearly understood with reference to the following examples; however, the examples are only intended to illustrate and not to limit the invention. All references to proportions will be in parts by weight unless otherwise indicated.

**Example I**

This example illustrates the preparation of a suitable enamel base. Eight parts of tung oil, 49.5 parts of linseed oil and 42.5 parts of Neville L-X-782 (petroleum hydrocarbon resin) are heated together at a temperature of 285° C. until the varnish reaches a viscosity of approximately "J" on the Gardner scale when reduced to 50%
non-volatile in mineral spirits. Heating is discontinued and the varnish is allowed to cool and is then reduced to 50% non-volatile in mineral spirits.

Example II

This example illustrates the preparation of the zinc paste. 56 parts of linseed oil acids are heated to 150° C. and 37.9 parts of dimerized rosin, 2 parts of maleic anhydride, and 4.1 parts of glycerin are added thereto. The mixture is heated to 235° C. and held at that temperature until the viscosity is G–H (Gardner scale) when reduced to 50% non-volatile in mineral spirits. The varnish is cooled and reduced to 50% nonvolatile in mineral spirits. The acid number of the varnish is less than 7.

53 parts of pure zinc oxide are dispersed in the above zinc paste varnish by grinding in a sand mill to produce a zinc paste containing 40% zinc oxide.

Example III

This example illustrates the preparation and use of the single package “C” enamel of the present invention. 100 parts of the reduced base varnish produced by Example I, 50 parts of the zinc paste produced by Example II, 1% manganese napthenate drier (1% metal) and 2.5 parts lubricant (40% petroleum wax in petroleum solvent) are blended together by milling for 15 minutes on a roll mill to produce the improved single package “C” enamel. This “C” enamel so produced has a storage stability of greater than six months.

The “C” enamel was coated in thin films of 412 to 612 milligrams per square inch dry film weight on flat stock of black plate tin plate and aluminum plate at bakes ranging from 6 to 12 minutes at 410° F. (or at shorter bakes at higher temperatures.) The resultant film is a gold amber color and is suitable for use as the sole internal lining in cans which contain wet foodstuffs.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

We claim:

1. A process for preparing a single package “C” enamel which comprises blending together (1) a petroleum hydrocarbon resin containing unsaturation and having a saponification number of less than 0.5 and an acid number of less than 0.5 modified with a drying oil and (2) a zinc paste made by grinding zinc oxide into a maleic anhydride-dimerized rosin product modified with an oil acid and tung oil, dehydrated castor oil or mixtures thereof and neutralized with a polyhydric alcohol.

2. The process of preparing a single package “C” enamel according to claim 1 comprising (a) preparing an enamel base by heating about 40 to 50 percent by weight of a petroleum hydrocarbon resin containing unsaturation and having a saponification number of less than 0.5 and an acid number of less than 0.5 and about 50 to 60 percent by weight of at least one drying oil at a temperature of about 150 to 300° C. until a viscosity of G to K (Gardner scale), when reduced to 50% non-volatile in mineral spirits, is obtained, (b) preparing a zinc paste varnish by reacting together 34 to 44 percent by weight of a dimerized rosin, 5 to 2.0 percent by weight of maleic anhydride, 45 to 56 percent by weight of member selected from the groups consisting of the oil acids of linseed oil, tung oil, dehydrated castor oil and mixtures thereof and 4.1 to 10 percent by weight of at least one polyhydric alcohol, a total weight of the zinc paste varnish, at a temperature of about 250 to 290° C. until a viscosity of G–H (Gardner scale) when reduced to 50% non-volatile in mineral spirits is obtained, (c) preparing a zinc paste by dispersing from about 30 to about 80% by weight of zinc oxide in said zinc paste varnish, and (d) preparing said single package “C” enamel by mixing said enamel base and 5 to 50 percent by weight, based on the total combined weight, of said zinc paste, wherein the single package “C” enamel so produced has at least six months’ storage stability.

3. The process of claim 2 wherein 1 to 25 percent by weight of zinc oxide is present in said single package “C” enamel.

4. The process of claim 2 wherein the drying oil is selected from the group consisting of linseed oil, tung oil, fish oil and mixtures thereof and wherein the polyhydric alcohol is selected from the group consisting of glycerol and pentaerythritol and mixtures thereof.

5. The process as claimed in claim 4 wherein the petroleum hydrocarbon resin and the drying oil are heated at a temperature of about 260 to 290° C.

6. A single package “C” enamel comprising a blend of (1) a petroleum hydrocarbon resin containing unsaturation and having a saponification number of less than 0.5 and an acid number of less than 0.5 modified with a drying oil and (2) a zinc paste made by grinding zinc oxide into a maleic anhydride-dimerized rosin product modified with an oil acid of linseed oil, tung oil, dehydrated castor oil or mixture thereof and neutralized with a polyhydric alcohol.

7. A single package “C” enamel according to claim 6 and essentially of (a) 50 to 95 percent by weight of an enamel base prepared by reacting 40 to 50 percent by weight of a petroleum hydrocarbon resin, having a saponification number of less than 0.5 and an acid number of less than 0.5 and 50 to 60 percent by weight of a drying oil until a Gardner scale viscosity of G to K, when reduced to 50% non-voltile in mineral spirits, is obtained, and (b) 5 to 50 percent by weight of a zinc paste prepared by mixing together 30 to 80 percent by weight of zinc oxide and 20 to 70 percent by weight of zinc paste varnish prepared by reacting together 34 to 44 percent by weight of a dimerized rosin, 5 to 2.0 percent by weight of maleic anhydride, 45 to 56 percent by weight of a drying oil acid and 4.1 to 10 percent by weight of at least one polyhydric alcohol until a Gardner scale viscosity of G–H when reduced to 50% non-voltile in mineral spirits, is obtained, wherein the single package “C” enamel has at least six months’ storage stability.

8. The single package “C” enamel as claimed in claim 7 wherein the drying oil is selected from the group consisting of tung oil, linseed oil, fish oil and mixtures thereof.

9. The single package “C” enamel as claimed in claim 8 wherein the enamel base is prepared by heating the petroleum hydrocarbon resin and the drying oil at a temperature of about 260 to 290° C., and the Gardner scale viscosity of the enamel base is about “J,” when reduced to 50% non-volatile in mineral spirits.

10. The single package “C” enamel as claimed in claim 7 wherein the polyhydric alcohol is selected from the group consisting of glycerol and pentaerythritol and mixtures thereof.

11. The single package “C” enamel as claimed in claim 7 wherein said drying oil acid is selected from the group consisting of the linseed, tung, dehydrated castor oil acids and mixtures thereof.

References Cited

UNITED STATES PATENTS

2,039,364 5/1936 Thomas et al. 260—23,7
2,069,247 2/1957 Hug 117—134
2,412,578 12/1946 Morrell 220—64
2,652,342 9/1953 Gleason 117—132
2,842,285 7/1958 Sackett 220—64
2,888,417 5/1959 Crouch 260—22
2,952,646 9/1960 Carmony 260—23,7

DONALD E. CZAJA, Primary Examiner.
R. W. GRIFFIN, Assistant Examiner.
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