PATENT SPECIFICATION (11) 1 575 121

1 575 121

(21) Application No. 9202/77 (22) Filed 4 March 1977
(31) Convention Application No. 664232
(32) Filed 5 March 1976 in
(33) United States of America (US)
(44) Complete Specification published 17 Sept. 1980
(51) INT CL³ C08L 83/04 B05D 5/08 (C08L 83/04 63/02)
(52) Index at acceptance
C3T 6F1 6J2C 6J3E 6J5 6J6
B2E 1711 409S 438T 448T M
C3B 1C22 1C25 1C6B 1C8T 1C9A 1C9B 1D2C 1L2X 1L6G M
C3Y B160 B230 B240 B245 F104 F583 F585

(72) Inventor DAVID KENNIT WALD

(54) COATING COMPOSITION COMPRISING A SILICONE RESIN, AN EPOXY RESIN, A SILICONE FLUID, AND A CATALYST

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a coating composition that is useful as a release finish for cooking vessels because of its thermal stability, release properties, hardness, glossy appearance and abrasion resistance. Particularly, this invention relates to a coating composition useful for coating tin-plated steel cooking vessels because it is curable at a temperature which is lower than the melting point of tin.

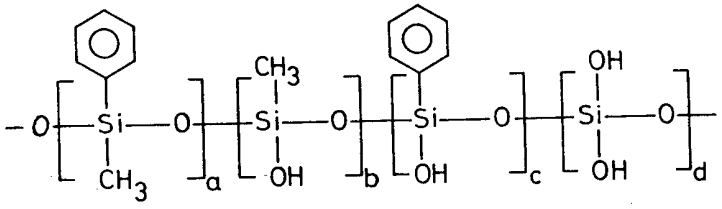
Cookware and bakeware items have been coated with fluorocarbon polymers, such as polytetrafluoroethylene and copolymers thereof. Finishes of polytetrafluoroethylene have excellent thermal stability and good release properties and have been widely used and well accepted. However, a primer is generally required for these coatings, along with special treatment of the metal substrate, to obtain excellent adhesion of the coating. Additionally, since the temperature needed to fuse the fluorocarbon polymer is higher than the melting point of tin, it cannot be used upon tin-plated metals. Therefore, it would be desirable to have a coating composition that could be applied to unprimed metal substrates, including tin, and would form a finish that has release properties and also good abrasion and scratch resistance.

The novel coating composition of this invention can be applied directly to metal without the use of a primer, forms a finish that has release properties, outstanding adhesion to unprimed metal, thermal stability, good hardness, abrasion resistance, and glossy appearance and is an ideal coating composition for cooking vessels, particularly tin-plated ones.

The coating composition has a solids content of 25—80% by weight in an inert liquid carrier and is comprised of

(a) a binder comprised of

(1) 60—90% by weight, based on the weight of the binder, of a silicone resin which is a heat curable methylphenyl polysiloxane resin having an average empirical formula



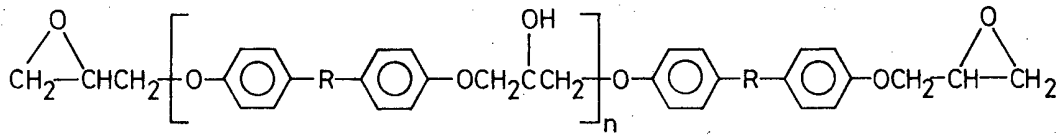
wherein

a, *b*, *c*, and *d* are positive integers which are sufficienlty large to provide the

resin, when measured at 60% resin solids in xylene at 25°C, with a viscosity of 30—50 centipoises, a specific gravity of 1.03—1.2, and a refractive index of 1.45—1.57, and having

a silanol content above 4% based on the weight of the resin;

(2) 1—40% by weight, based on the weight of the binder, of an epoxy resin having the formula:



wherein *n* is an integer from 0—42, and R is an alkylene group of 1—4 carbon atoms;

(b) 0.2—10% by weight, based on the weight of the binder, of silicone fluid which is a dimethyl polysiloxane fluid having a viscosity of 50—5000 centistokes measured at 25°C;

(c) 0.2—10% by weight, based on the weight of the binder, of catalyst which is a metal salt; and

(d) inert liquid carrier.

A metal cooking vessel coated with a cured film produced by the above composition is also part of the invention.

The coating composition of this invention preferably has a relatively high solids content of about 20—70 percent by weight in a suitable liquid carrier. The film-forming binder constituents are suitably dissolved in organic solvents such as toluene, xylene, tetrahydrofuran, butyl carbitol, ethylene glycol monoethyl ether and ethylene glycol monobutyl ether.

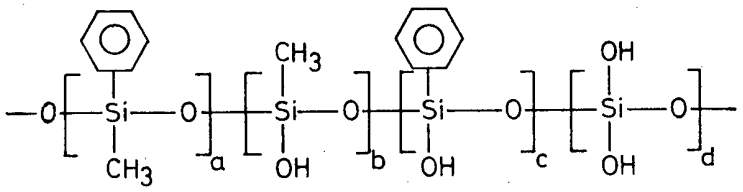
The binder of the novel coating composition of this invention is a blend of silicone resin which is a highly reactive methylphenyl polysiloxane and an epoxy resin. The binder contains 60—99 percent by weight of silicone resin and 1—40 percent by weight epoxy resin in the amounts necessary to total 100 percent. Preferably, the binder contains 90—99 percent by weight of silicone resin and 1—10 percent by weight of epoxy resin.

Also present in the composition is a silicone fluid which is a dimethyl polysiloxane. The amount of dimethyl polysiloxane fluid utilized is based on the total weight of binder. The amount of fluid will range from 0.2—10% by weight, based on the weight of the binder; preferably, the range will be 1—3% by weight.

A catalyst is added to the composition to ensure good film formation and rapid cure. The amount of catalyst utilized is also based on the total weight of binder. It will range from 0.2—10% by weight, based on the weight of the binder; preferably, the weight will be 0.4—1.2% by weight.

The combination of these components provides a coating composition that adheres well to unprimed metal substrates in combination with good release properties, desirable thermal stability, and low temperature cure.

The highly reactive methyl phenyl polysiloxane resin is heat curable, has a silanol content above 4%, preferably 5%, based on the weight of the resin, and has an average empirical formula:



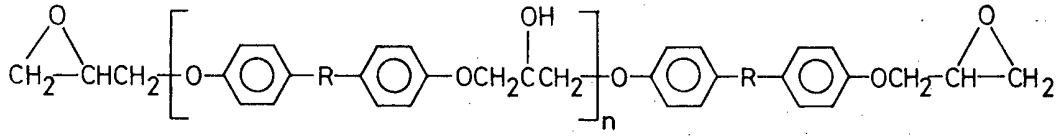
wherein

a, b, c, and *d* are positive integers which are sufficiently large to provide the resin, when measured at 60% resin solids in xylene at 25°C, with a viscosity of 30—50 centipoises, a specific gravity of 1.03—1.2, and a refractive index of 1.45—1.57.

A particularly preferred methyl phenyl siloxane resin, when measured at 60% solids in xylene at 25°C, has a viscosity of 35—45 centipoises, and has a specific

gravity of 1.05—1.12, and a refractive index of 1.50—1.53; it also has a softening point of 75—85°C.

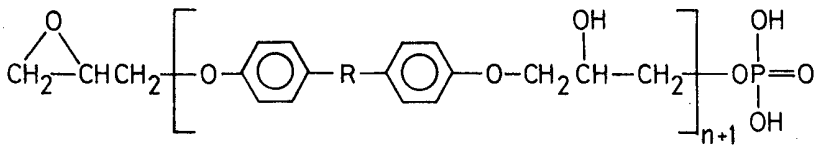
The epoxy resins utilized in the present invention are commonly known in the art. One class of such resins has the generalized formula



where *n* is an integer from 0—42 and R is an alkylene group of 1—4 carbon atoms. The epoxy resins utilized in the present invention contain at least two epoxy groups per molecule and therefore, upon curing of the composition, introduce no uncross-linkable extractable portions into the coating.

Preferably, to obtain a coating with high gloss, a liquid epoxy resin is used. An undiluted liquid epoxy resin where the average value of *n* is about 0—3, R is isopropylidene, the viscosity is 1.2—225 poises at 25°C as measured by ASTM-D-445, and the epoxy equivalent about 150—470 is preferred. The epoxy equivalent is defined as the grams of resin containing one gram-equivalent of epoxide functionality as measured by ASTM-D-1652. A coating composition containing "Epon 828" is particularly preferred because finishes produced by such compositions have high gloss while maintaining high adhesion. "Epon" is a registered Trade Mark. "Epon 828" is a liquid epoxy resin where the average value of *n* is about 0, R is isopropylidene, the viscosity of the undiluted resin is 100—160 poises at 25°C as measured by ASTM-D-445, and the epoxy equivalent is 185—192.

Modifications of epoxy resins can also be utilized in the coating composition of the present invention. For example, it is known to those skilled in the art that when an epoxy compound containing a hydroxy group is brought in contact with an acid, there results an ester or mixture of esters, Thus, when phosphoric acid is added to an epoxy resin, a reaction occurs at one or more of the epoxy groups of the molecule and the resulting mixture contains both the mono- and diesters of phosphoric acid. A product of this reaction is exemplified by the formula



These modified epoxy resins can still function as epoxy resins in the coating compositions of the invention.

The dimethyl polysiloxane fluid utilized in the coating composition of this invention can have a viscosity of 0.65 to over a million centistokes measured at 25°C, but preferably has a viscosity of 100—5000 centistokes. To form particularly high quality compositions, a viscosity of 500—1500 centistokes is preferred. The dimethyl polysiloxane fluid is used to increase the release characteristic of the film produced.

Catalysts useful in the coating composition of this invention are metal salts, particularly metal salts of fatty acids such as zinc octoate and cobalt naphthenate. A preferred zinc octoate is Nuodex, registered Trade Mark (a zinc octoate solution having an 8% zinc metal content sold by Tenneco). A coupling solvent, such as V.M. and P. Naptha, is sometimes used to ensure solubility of the catalyst within the coating composition.

Suitable liquid carriers include such organic solvents as those used for dissolving the film-forming binder constituents, for example, toluene, xylene, tetrahydrofuran, butyl carbitol, ethylene glycol monoethyl ether and ethylene glycol monobutyl ether.

Optionally, pigments can be used in the coating composition of the invention. A ratio of pigment to binder of about 1/100—400/100 can be utilized, preferably, about 1/100—200/100, more preferably, in compositions having excellent properties, about 1/100—50/100. Typical pigments that can be used are, for example, carbon black, titanium dioxide, brown, black, and yellow iron oxides, aluminum silicate, mica, talc, china clay, metal powders and carbonates.

Optionally, to provide the composition with increased scratch resistance, abrasion resistance, hardness, blister resistance and decreasing porosity, finely

divided inorganic hardening fillers may be added in a ratio of hardening filler to binder of about 5/100 to about 400/100. The hardening fillers that can be used include zirconium silicate, zirconium oxide, silicon dioxide, reactive and unreactive aluminas, and filler pigments such as aluminum flake, potassium titanate fibrils, titanium dioxide fibrils, silicone dioxide fibrils, and alumina monohydrate fibrils. Examples of aluminas which can be used are calcined aluminas, low-soda aluminas, reactive aluminas, high-purity aluminas, tabular aluminas, calcium aluminate cement, and hydrated alumina. The preferred hardening fillers are reactive alumina. A preferred reactive alumina which is useful as a coating composition having excellent properties is "Reactive Alumana A-15SG" which is solid by Alcoa. This alumina consists of

Al_2O_3	99.5+%
Na_2O	.08
SiO_2	.07
Fe_2O_3	.01

It, with compaction and sintering aids, can provide an all-alumina composition with a green body density of 2.86 gm/cc at 5000 psi, and fired density of 3.93 gm/cc, with only 10.1 percent linear shrinkage after one hour at 1665°C.

When a reactive alumina is used as the hardening filler, its ratio to binder is about 10/100 to about 70/100; preferably 20/100 to 40/100.

The coating composition of this invention can be prepared by many methods known to the artisan. One method is to first prepare a mill base by mixing pigment, silicone fluid, solvent, and silicone resin and then grinding the mixture by conventional techniques such as pebble mill grinding, ball mill grinding and sand mill grinding. To the mill base is added more silicone resin and solvent, epoxy, catalysts and other constituents; this is blended to form the coating composition.

The composition of this invention is applied to the interior of a vessel by first roughening the interior surface of the vessel, preferably by grit blasting the surface with grit, or the surface can be roughened by other techniques. The surface is then cleaned.

The coating composition of this invention is then applied by conventional techniques, such as, spraying, electrostatic spraying and roller coating to the surface of the vessel to a thickness of 0.2—5 mil (dry), preferably 0.5—1.5 mil (dry) and is then baked for about 5—45 minutes at about 175—400°C.

The coating composition of this invention forms excellent finishes, not only on cooking vessels, but also on ice cube trays, dough cutters, paper cutters, and can be used as a lubricant coating on bearing and curtain rods and can be used as a coating on coin machine slots, fan vents, shovels, and discardable aluminum utensils.

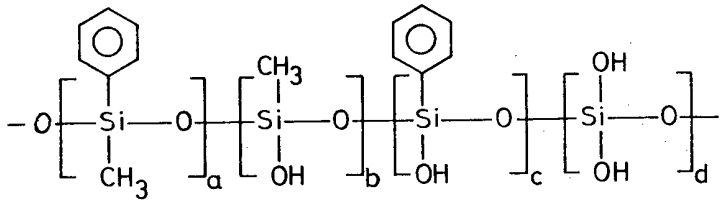
The following example illustrates the invention. All quantities are on a weight basis unless otherwise indicated.

EXAMPLE

A coating composition was prepared as follows:

(a)(1) Preparing a resin solution by mixing until dissolved:

	Parts by Weight
Silicone resin flake which is a heat curable methyl phenyl polysiloxane resin having an average empirical formula	



wherein *a*, *b*, *c*, and *d* are positive integers which are sufficiently large to provide the resin, when measured at 60% resin solids in xylene at 25°C, with a viscosity of 40 centipoises, specific gravity of 1.08, and refractive index of 1.518, and having a silanol content above 5% based on the weight of the resin 20.00

Xylene 20.00

and

(2) adding to the product of (a)(1) and then grinding for 16 hours:

	Parts by Weight
Xylene	56
Titanium dioxide pigment	100
Silicone fluid (D.C. 200, a polydimethyl siloxane having a viscosity at 25°C of 1000 centistokes, sold by Dow Corning)	2.0

(b) adding to the mill base of (a), the following and mixing until dissolved:

	Parts by Weight
Silicon resin flake (described in (1))	455
Xylene	455

(c) Adding the following to the produce of (b) and then blending together:

	Parts by Weight
"Epon 828" (a liquid epoxy resin sold by Shell Chemical Company)	25
Cobalt naphthenate	7.05
"Nuodex" (a zinc octoate solution, having 8% zinc metal content sold by Tenneco	9.25
V.M. and P. Naptha	50
	1201.30

A tin plated steel muffin pan was wiped with xylene to remove any residue grease and then was grit blasted with 200 mesh grit at 80 pounds per square inch. The pan was then cleaned of grit particles with a blast of compressed air and was wiped with xylene.

The coating composition was then sprayed onto the pan to a film thickness of 0.7 mil (dry) and air dried for 10 minutes and then baked for 15 minutes at 215°C.

The resulting finish on the pan had a good glossy appearance, excellent adhesion to the metal substrate, a pencil hardness of F, and was fully curred as measured by a 50 double wipe test with toluene.

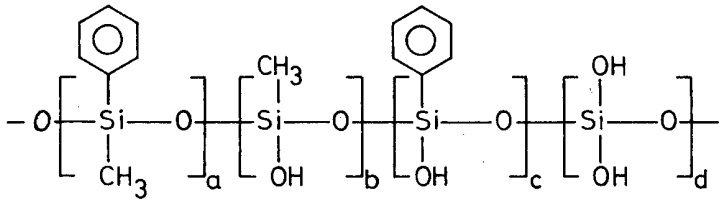
The coated pan was subjected to a 10 bake test at 220°C with blueberry muffin mix and meat loaf mix. the release properties, ease of cleaning, and appearance of the finish remained excellent.

WHAT WE CLAIM IS:—

1. A coating composition having a solids content of 25—80% by weight in an inert liquid carrier and comprised of

(a) a binder comprised of

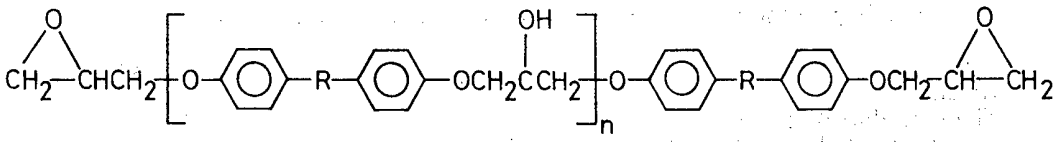
(1) 60—99% by weight, based on the weight of the binder, of a silicone resin which is a heat curable methylphenyl polysiloxane resin having an average empirical formula



wherein

a, b, c and *d* are positive integers which are sufficiently large to provide the resin, when measured at 60% resin solids in xylene at 25°C, with a viscosity of 30—50 centipoises, specific gravity of 1.03—1.2, and refractive index of 1.45—1.57, and having a silanol content above 4% based on the weight of the resin;

(2) 1—40% by weight, based on the weight of the binder, of an epoxy resin having the formula:



wherein
n is an integer from 0—42, and
R is an alkylene group of 1—4 carbon atoms;

(b) 0.2—10% by weight, based on the weight of the binder, of a silicone fluid which is dimethyl polysiloxane fluid having a viscosity of 50—5000 centistokes measured at 25°C;

(c) 0.2—10% by weight, based on the weight of the binder, of catalyst which is a metal salt; and

(d) inert liquid carrier.

2. The coating composition of Claim 1 wherein the binder comprises

(a) 90—99% by weight, based on the weight of the binder, of silicone resin, and

(b) 1—10% by weight, based on the weight of the binder, of epoxy resin.

3. The coating composition of Claim 1 or 2 containing

(a) 1—3% by weight, based on the weight of the binder, of said silicone fluid, and

(b) 0.4—1.2% by weight, based on the weight of the binder, of catalyst.

4. The coating composition of Claim 1, 2 or 3, wherein the silicone resin has a silanol content above 5%, based on the weight of the resin,

a softening point of 75—85°C, and, when measured at 60% resin solids in xylene at 25°C, a viscosity of 35—45 centipoises,

a specific gravity of 1.05—1.12, and

a refractive index of 1.50—1.53.

5. The coating composition of any one of Claims 1 to 4 wherein the epoxy resin is a liquid

having a viscosity of 1.2—225 poises at 25°C, an epoxy equivalent of 150—470; and

wherein *n* is an integer from 0—3, and R is isopropylidene.

6. The coating composition of any one of Claims 1 to 5 wherein the silicone fluid has a viscosity at 25°C of 500—1500 centistokes.

7. The coating composition of any one of Claims 1 to 6 wherein the catalyst is a metal salt of a fatty acid.

8. The coating composition of any one of Claims 1 to 7 containing pigment in a pigment to binder ratio of about 1/100 to 400/100, and inorganic hardening agent in a hardening agent to binder ratio of 5/100 to 400/100.

9. The coating composition of any one of Claims 1 to 8 wherein

(a) the binder is comprised of

(1) 90—99% by weight, based on the weight of the binder, of a silicone resin having

(a) a silanol content above 5% based on the weight of the resin,

(b) a softening point of 75—85°C, and

(c) when measured at 60% resin solids in xylene, a viscosity of 35—45 centipoises, a specific gravity of 1.05—1.12, and a refractive index of 1.50—1.53; and

(2) 1—10% by weight, based on the weight of the binder, of liquid epoxy resin having a viscosity of 1.2—225 poises at 25°C, and an epoxy equivalent of 150—470; and wherein *n* is an integer from 0—3, and R is isopropylidene;

(b) 1—3% by weight, based on the weight of the binder, of a silicone fluid having a viscosity of 500—1500 at 25°C;

(c) 0.4—1.2%, by weight, based on the weight of the binder, of a catalyst which is a metal salt of a fatty acid;

(d) pigment in a pigment to binder ratio of 1/100 to 400/100;

(e) an inorganic hardening filler as a hardening filler to binder ratio of 5/100 to 400/100; and

(f) an inert liquid carrier.

11. A coating composition according to any one of the preceding claims wherein the epoxy resin component of the binder has been modified.

12. A coating composition according to Claim 1 substantially as described herein and exemplified.

13. A cooking vessel coated with a film produced by curing the coating composition of any one of the preceding claims.

14. A metal article coated with the coating composition of any one of Claims 1 to 12.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43 Bloomsbury Square,
London WC1A 2RA.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.