PATENT SPECIFICATION

(11) 1 565 698

1 565 698

(21) Application No. 23121/78 (22) Filed 13 Sept. 1976
(62) Divided out of No. 1565697
(31) Convention Application No. 616513
(32) Filed 25 Sept. 1975
(31) Convention Application No. 616530
(32) Filed 25 Sept. 1975 in
(33) United States of America (US)
(44) Complete Specification published 23 April 1980
(51) INT CL^3 C09D 3/80 B32B 15/08 (C09D 3/80 3/52 3/58)
(52) Index at acceptance
C3B 1D2C 1N1A 1N1F 1N2A 1N4C 1N7 1N9X EX
B2E 407S 409S 412S 448T 450T 454BT 480BT ANA

(19) THE PATENT OFFICE LONDON

(54) ENAMEL COATING COMPOSITION

(71) We, THE CONTINENTAL GROUP, INC., a corporation organized and existing under the laws of the State of New York, United States of America, of 633 Third Avenue, New York, New York, 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 generally to adhering a propylene polymer layer to an enamel coated metal surface and more particularly to an enamel coating composition for coating such a metal surface.

Easy opening containers are known to the art. These containers are generally formed of metal and are provided with at least one pour opening. The pour opening generally occupies only a portion of the end panel of the container. Heretofore, the pour opening has generally been formed by scoring to define a tear strip. A pull tab is attached to the tear strip, and upon the application of a force, the pull tab is operative to separate the tear strip from the panel along the score line.

Although easy opening containers have been readily accepted by the public, deficiencies still remain in this kind of container. One of these deficiencies is that the removable tear strip which is torn from the end panel in the opening of the can has sharp edges, and when thrown on the ground or otherwise improperly disposed of, remains as a nuisance which presents a cutting hazard to the public.

It has been proposed e.g., British Patent Specification No. 1257620, to replace the metal tear strip with a plastics layered closure member to eliminate the cutting hazard as the removed portion will not have sharp edges. The closure member fabricated entirely from a thermoplastics resin, such as polypropylene, or a laminate of the resin and a metal foil such as aluminum or steel, is heat sealed to the surface of an enamel coated end panel having at least one preformed opening, the enameled surface of the panel having been coated with a heat activatable, bond promoting layer containing a carboxyl modified polypropylene resin.

Although the plastics containing closures of British Patent Specification No. 1257620 could be effectively bonded to the metal can ends, problems arose in the application of the carboxyl modified polypropylene layer to the enamelled metal surface.

When the carboxyl modified polypropylene resin is utilized as an adhesion promoting layer for bonding the propylene polymer layer of a closure member to an enamel coated metal can end, the carboxyl modified polypropylene resin is usually applied as a dispersion in a volatile organic solvent such as kerosene. The carboxyl modified polypropylene resin used to prepare the dispersion generally has a particle size of 0.1 to 5 microns and is at the present time a relatively expensive resin material. Although only small amounts of the modified resin are required in the adhesion promoting layer, the application of the modified resin in a dilute dispersion e.g., 10% solids in unsatisfactory as such dilute dispersions do not have the required physical properties such as viscosity and flow out, which are required for the application of the coating dispersion using conventional coating equipment, e.g. as by roll coating. To obtain a coating dispersion having the properties necessary for commercial coating application, polypropylene resin powders of approximately the same particle size range, e.g. 0.1—5 microns are incorporated in the dispersion to raise the solids content to about 20% whereby the dispersion has the flow and viscosity characteristics required in commercial coating methods. One drawback to the use of polypropylene resins of such particle size is that the submicron size resin is difficult to manufacture and is presently in limited commercial supply.

According to the present invention there is provided an enamel coating composition comprising a carboxyl modified polypropylene resin incorporated into an epoxy resin enamel coating formulation containing a heat-activatable aminoplast cross-linking resin.

In a preferred enamel coating composition the cross-linking resin is a urea-formaldehyde resin. Preferably the solids content of the composition comprises 60 to 95% by weight of the epoxy resin, 5 to 40% by weight of the urea-formaldehyde resin, and 0.01 to 5% by weight of the carboxyl modified polypropylene resin, more preferably the solids content of the composition comprises 70 to 90% of the epoxy resin, 5 to 25% by weight of the urea-formaldehyde resin and 0.1 to 5% by weight of the carboxyl modified polypropylene resin.

Preferably, the carboxyl modified polypropylene resin is the reaction product of polypropylene and an unsaturated dicarboxylic acid or anhydride, e.g. maleic anhydride, and contains 0.1% to 5.0% by weight of carboxyl groups.

The enamel coating compositions according to the present invention can be applied to a metal surface, such as a metal sheet intended to form the end panel of an easy opening container, whereupon the coated metal surface is baked to cure and harden the coating composition. It is then possible to attach a layer of a propylene polymer directly to this enamel coated metal surface by heat-sealing the propylene polymer layer thereto. The method of bonding such a propylene polymer layer to such a metal surface is described and claimed in our Application No. 37898/76. The propylene polymer layer alone can be used as a closure member for an easy opening container, or it may form part of a laminate of a metal foil and the propylene polymer layer.

To form a dispersion of the coating composition, preferably the carboxyl modified polypropylene resin is added to an enamel coating formulation while said resin is dissolved in a solvent which is an organic acid or an alcohol or a hydrocarbon having at least 10 carbon atoms, or a mixture thereof, the solvent preferably being heated to a temperature above 100°C at the time of addition.

The amount of carboxyl modified polypropylene incorporated in the enamel coating composition is preferably in the range of 0.01 to 5 percent, more preferably 0.1 to 3 percent, by weight of the solids content of the enamel coating composition.

The coating composition according to the invention eliminates the necessity for the application of special polypropylene/carboxyl modified polypropylene layers to enamelled metal surfaces to enable propylene polymer layers to be attached by heat sealing to the enamelled metal surfaces.

By the use of the coating compositions according to the invention, propylene polymer layers can be bonded directly to enamel coated metal surface without the need for a separate adhesion promoting layer between the propylene polymer layer and the enamel coated metal layer as has been the practice of the prior art.

The present invention will now be described, by way of example, with reference to the accompanying drawings, in which:—

Figure 1 is a top plan view of a container having an easy opening structure provided with a laminated closure member containing a propylene polymer layer secured to an end panel surface coated with an enamel coating formed from a composition of the invention,

Figure 2 is an enlarged cross-sectional view taken generally along the line 2—2 of Figure 1,

Figure 3 is an elevational view of a container having a lapped side seam,

Figure 4 is a cross-sectional view taken along the line 4—4 of Figure 3 showing the sideseam in detail.

The carboxyl modified polypropylene which is used in the compositions of the present invention can be prepared by grafting an unsaturated dicarboxylic acid or anhydride onto a polypropylene backbone using high energy radiation or a peroxy catalyst as described in British Patent Specification No. 1,020,740. Unsaturated dicarboxylic acids or anhydrides which can be employed to prepare the carboxyl modified polypropylene resins include maleic, tetrahydrophthalic acid, fumaric acid, itaconic, nadic, methyl nadic and their anhydrides, maleic anhydride being preferred.

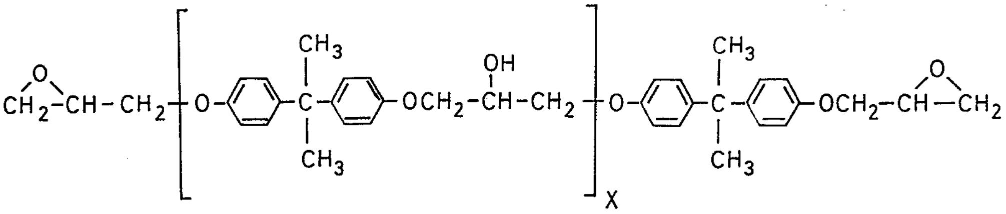
The amount of unsaturated dicarboxylic acid or anhydride which can be grafted onto the polypropylene backbone preferably ranges from 0.05 to 10 percent by weight based on the total weight of the grafted polymer and more preferably the amount of grafted dicarboxylic acid or anhydride ranges from 0.1 to 5.0 percent, most preferably from 0.5 to 5.0 percent.

When the carboxyl modified polypropylene resin is utilized as an adhesion promoting adjuvant for enamel coating, the resin can be of any particle size; the particle size is generally from 0.05 to 50 microns, more preferably from 35 to 40 microns.

The enamel coating in which the carboxyl modified polypropylene resin is incorporated is an epoxy resin coating formulation containing a heat activatable aminoplast cross-linking resin.

The preferred aminoplast condensates are urea-aldehyde and triazine aldehyde resins and alcohol modified derivatives thereof, that is, alkylated amino resins wherein the alkyl radical contains from 2 to 8 carbon atoms. Such aminoplast resins are the reaction products of aldehydes, for instance formaldehyde or acetaldehyde with urea, substituted ureas, thioureas, ethylene urea, melamine, benzoguanamine or acetoguanamine. The resulting methylol substituted products are etherified with alcohols, for example isopropanol, butanol and 2-ethyl hexanol, in order to obtain stability and organic solubility. Such organic soluble aminoplast resins are contemplated for use in this invention, butylated urea formaldehyde resins being preferred.

The epoxy resins used for preparing the enamel compositions are the polymeric reaction products of polyfunctional halohydrins with polyhydric phenols. The preferred epoxy resins have the structural formula:



wherein X represents the number of molecules condensed. Typical polyfunctional halohydrins are epichlorohydrin and glycerol dichlorohydrin. Typical polyhydric phenols are resorcinol and a 2,2-bis(4-hydroxyphenyl) alkane, the latter resulting from the condensation of phenols with aldehydes and ketones, including formaldehyde, acetaldehyde, propionaldehyde, acetone and methyl ethyl ketone, which result in such compounds as 2,2-bis(4-hydroxyphenyl)propane. These epoxy resins normally contain terminal epoxy groups but in some instances they may contain terminal epoxy groups and terminal hydroxyl groups.

The molecular weight of the epoxy resins may be controlled by the relative proportions of the reactants as well as by the extent to which the polymerisation reaction proceeds.

It is preferred that epoxy resins which are of relatively high molecular weight are utilized in preparing the enamel coatings. Generally, epoxy resins having an average molecular weight in the range of 1400 to 5000 may be used.

Epoxy resins are available commercially. Preferred examples are EPON 1004 and EPON 1007, products of Shell Chemical Company, which are the condensation products of epichlorohydrin and Bisphenol A (dihydroxy-diphenyl-dimethyl methane) and have respective epoxy assays of 875 to 1025 and 2500 to 4000 grams of sample per gram mole of epoxy group (gram/gram mole). In general, the average molecular weight of an epoxy resin is approximately twice the epoxy assay.

The solids content of the enamel coated composition of the present invention comprises 60 to 95, preferably 70 to 90, percent by weight of the epoxy resin; 5 to 40, preferably 10 to 30, percent by weight of the aminoplast resin; and 0.01 to 5, preferably 1.0 to 3, percent by weight of the carboxyl modified polypropylene resin.

Generally, to prepare the enamel composition of the present invention, the epoxy resin and aminoplast resin are dissolved in a mixture of solvents such as a mixture of a ketone and an aromatic hydrocarbon until the resins are completely dissolved.

Examples of ketones which can be employed as solvents for the epoxy resin aminoplast resin-based enamel coating formulations include methyl ethyl ketone, methyl isobutyl ketone, isophorone, cyclohexanone, diacetone alcohol and diisobutylketone. Examples of aromatic hydrocarbon useful as solvents for epoxy resin aminoplast resin based-enamel coating formulations include benzene, toluene, xylene, and commercially available aromatic naphtha mixtures, such as "Solvesso" 100 to 150. "Solvesso" is a registered Trade Mark. Other useful solvents are ether alcohols such as butyl cellosolve and ether alcohol esters such as "Cellosolve" acetate.

Antioxidants and thermal stabilizers may also be incorporated in the enamel coating composition to inhibit oxidation of the carboxyl modified polypropylene resin during the baking and curing of the enamel coating after its application to a metal surface. Antioxidant compounds which have been found useful include hindered phenolic compounds such as Irganox 1010, tetrakis [methylene 3-(3′,5′-di-tert-butyl-4-hydroxyphenyl) propionate]; these antioxidants are usually incorporated in the enamel coating compositions at concentrations in the range of 0.1 to 1.0% by weight based on the solids content of the enamel. Lubricants, such as polyethylene dispersions, which are required during forming of the enamel coated metal sheet in container end manufacture may also be incorporated in the enamel.

To improve the heat sealability of the baked enamel composition, the carboxyl modified polypropylene resin is preferably first dissolved in a hot, e.g. greater than 100°C organic solvent which is an aliphatic compound containing at least 10 carbon atoms such as an alcohol, an acid or a hydrocarbon.

As will hereinafter be illustrated if a solvent other than an aliphatic compound containing at least 10 carbon atoms is used as a solvent for the carboxyl modified polypropylene resin in this preferred procedure, the incorporation of the modified polypropylene resin in an enamel formulation dissolved in such solvents will not materially improve the heat seal bond between a propylene polymer and the baked enamel coating.

In preparing solutions of the carboxyl modified polypropylene resin for incorporation in the enamel coating formulation by the preferred procedure, the resin is added to the organic alcohol, acid or hydrocarbon solvent at a concentration of 1 to 30% by weight, preferably 2 to 10% by weight. After the resin is added to the solvent, the resultant mixture is heated to a temperature above 100°C until the resin completely dissolves in the solvent. The resin solution is then added to the enamel coating formulation, preferably one which is an organic solvent solution of the said epoxy resin and a cross-linking material such as the said heat activatable aminoplast resin. It is preferred that the resin solution be at a temperature above 100°C when added to the enamel coating formulation. As will hereinafter be illustrated, if the temperature of the resin solution is 100°C or less, gel formation is observed and the strength of the heat seal bond which is subsequently obtained between the polypropylene polymer and enamel coated metal surface is materially diminished.

Examples of suitable organic alcohols used to prepare solutions of the carboxyl modified polypropylene resin for incorporation in the enamel coating formulations are long chain, saturated or unsaturated, aliphatic monohydroxy alcohols having a general formula R—OH wherein R is a straight or branched-chain saturated or olefinically unsaturated hydrocarbon group having from 10 to 30, preferably from 12 to 22, carbon atoms. Illustrative of such alcohols are decyl alcohol, tridecyl alcohol, lauryl alcohol, tetradecyl alcohol, cetyl alcohol, oleyl alcohol, linoleyl alcohol, palmitoleyl alcohol, arachidyl alcohol, stearyl alcohol, benhenyl alcohol, arachindonyl alcohol, myristoleyl alcohol and mixtures of these alcohols.

Examples of suitable organic acids which may be used as solvents for the carboxyl modified polypropylene resin are separated and olefinically unsaturated aliphatic acids having 10 or more carbon atoms, preferably 12 to 22 carbon atoms. Examples of such acids are the fatty acids: capric acid, lauric acid, myristic acid, palmitic acid, isostearic acid, stearic acid and arachidic acid, undecylemic acid, myristoleic acid, palmitoleic acid, oleic acid, cetoleic acid and erucic acid and mixtures of these acids.

Examples of suitable aliphatic hydrocarbons having 10 or more carbon atoms which may be used as solvents include saturated hydrocarbons such as decane, iodecane, pentadecane, nepthadecane, nonadecane and mixtures of such hydrocarbons such as kerosene and mineral oil, as well as unsaturated hydrocarbons and particularly unsaturated hydrocarbons having olefinic unsaturation such as undecene, tridecene and pentadecene, and mixtures thereof such as a mixture of C_{11} to C_{15}-olefinically unsaturated hydrocarbons.

The enamel compositions of this invention can be satisfactorily applied at a solids content ranging from 20% to 70% by weight, based on the total weight of the liquid coating composition. Generally, a solids content of 30 to 50% by weight is preferred.

The enamel coating composition containing the adhesion promoting carboxyl modified polypropylene resin can be satisfactorily applied by any of the conventional methods employed in the coating industry. However, for coating of sheet metal used in container manufacture, gravure or direct roller coating are preferred methods, as the desired coating weight is easily and conveniently applied in a single coat. Spraying, dipping and flow coating are also useful methods of applying the coating dispersion.

After applying the enamel coating, it is cured and hardened preferably by heating the coated substrate at a temperature of 350°F to 600°F for a period of 20 minutes to 1 minute, the preferred conditions being 8—10 minutes at 400°F.

The preferred coating weight for coating metal end panels to which a propylene polymer closure may be heat sealed is in the range of 2.5 to 10.0 milligrams of dry coating per square inch of substrate surface to provide an enamelled surface to which a propylene polymer layer can be heat sealed.

Propylene polymer layers which may be bonded to the enamel coated surface include polypropylene, and propylene/ethylene copolymers containing from 1% to 10% ethylene.

The propylene polymer layer is bonded to the enamel coated metal surface by heat sealing preferably at a temperature range of 350° to 450°F, more preferably at a temperature of 375° to 400°F. Heat sealing may be accomplished by any means known to the art, such as a hot platen press or metal jaws heated by resistance wire or by induction heating, using dwell times varying from 0.1 seconds to 5 seconds.

After the propylene polymer layer is heat sealed and bonded to the enamel coated metal surface, the assembly is allowed to cool to ambient temperature.

Referring to the drawing, and in particular to Figure 1, there is shown a container top end assembly 10 of a container. The end assembly 10 is made of metal such as tin plate, tin-free steel or aluminum. The end assembly 10 comprises a central panel 11 having a bead formed adjacent the outer periphery from which there depends a peripheral flange 12. The peripheral flange 12 is arranged to be curled and double seamed with an outwardly extending flange at the upper end of a container body in the usual manner.

The panel 11 in the embodiment illustrated in the drawing is shown with a plurality of pour openings 13 through which the contents of the container are poured.

It is to be understood that the openings 13 may assume any configuration, and is not limited to the pour opening arrangement shown in the drawings.

The top surface of the end assembly 10 is coated with a layer of the thermosetting enamel coating composition of the present invention, such as an epoxy-urea/formaldehyde resin 14 having incorporated therein an adhesion promoting carboxyl modified polypropylene resin, such as polypropylene/maleic anhydride graft copolymer. Peelably heat sealed to the enamel layer 14 is a laminated closure member 15 constructed of an aluminum foil outer layer 16 and a polypropylene inner layer 17. The closure member 15 has a sealing flap 18 for closing the openings 13. Integrally extending from the sealing flap 18 is a pull ring portion 19.

The peelable heat sealed bond that is formed due to the presence of the carboxyl modified polypropylene resin in the enamel layer 14 permits the flap 18 to be heat sealed to the metal end panel and thereafter separated cleanly from the metal and by the application of a pulling force at the ring portion 19. Preferably, the pull ring portion 19 is formed with an opening size to receive the finger of a user. The heat to achieve bonding is preferably applied by induction heating of the metal surface. In this manner, the sealing flap 18 is firmly heat sealed but peelably fixed about the openings 13 and remains adhered thereto until pulled and separated from the container end surface.

In addition to promoting the adhesion of propylene polymer coated closures to enamel coated container ends, the coating compositions of the present invention have other applications in the container fabrication art and the metal adhesion art generally.

Another example of the use of the compositions of the present invention in the container fabrication art is in the fabrication of container bodies. In one method of metal container body manufacture, a sheet of enamel coated metal is formed into a tubular shape and the edges of the blank are brought together in lapped relation. A sealed joint is made by interposing a bonding agent between the laps and then heating the joint and pressing the laps together to obtain the desired bond of the metal sections. Propylene polymers have not been utilized as adhesive materials due to their poor bonding adhesion to enamelled metal surfaces. By modifying the enamel coating applied to the blank with a carboxyl modified polypropylene resin to form a coating composition in accordance with the present invention and preparing an enamel coated metal sheet from this coating composition, the adhesion of propylene polymers to the enamelled metal surface is improved to a degree that the propylene polymer can be used as a bonding agent for the lapped portions of the container body.

Thus, in Figure 3, there is shown a container 20 having body 21, and end 22 and a longitudinal side seam 23. Figure 4 shows the side seam 23 in detail. The side seam is composed of metal layers 25, 26 each having applied thereto an enamel coating 27 according to the present invention. The seam 23 has a laminate structure consisting of the overlapped edges of enamel coated metal surfaces 25, 26 having a propylene polymer layer 28 interposed therebetween bonding the overlapped edges together.

To illustrate the manner in which the present invention may be carried out, the following Examples are given.

In the Examples, parts and percentages are by weight, unless specified otherwise.

EXAMPLE 1

An epoxy resin based enamel coating formulation was prepared composed of a 40% by weight solids consisting of 80 parts of the diglycidyl ether of Bisphenol A and 20 parts of a butylated urea formaldehyde suspended in an organic solvent mixture of approximately equal parts of xylene, methyl isobutyl ketone, diacetone alcohol and butyl alcohol.

To the enamel coating formulation was added Hercoprime A-35 (trademark) in the form of a 10% dispersion in kerosene. Hercoprime A-35 is a maleic anhydride modified polypropylene resin having an inherent viscosity of about 1.7, a carboxy content of 0.5% to 1.0%, a particle size range of 35 to 40 microns and a specific gravity of 0.9. The final solids content of the modified enamel formulation consisted of 98.5% by weight of the epoxy resin/urea formaldehyde enamel coating solids and 1.5% by weight of the Hercoprime A-35. In adding the Hercoprime dispersion to the enamel coating formulation, the Hercoprime dispersion was slowly added to the epoxy enamel formulation at ambient room temperature (25°C) and with vigorous stirring. Stirring of the modified enamel suspension was continued for another five minutes or until a homogeneous mixture has been achieved.

The Hercoprime modified enamel formulation was applied by means of a laboratory coating rod to the surface of a sheet of tin-free steel at a coating weight of 2.5 mgs/in^2. After application of the enamel coating formulation, the wet sheet was baked at 205°C for 8 minutes in a hot-air oven to volatize the solvent and cure the enamel to a hard film. Strips 4″×1″ were cut from the coated sheet to test the bonding characteristics of the enamel. A similar sized strip of a polypropylene/aluminum foil laminate constructed of 4 mil aluminum foil having adhered thereto a 2 mil polypropylene resin having a melt index 0.5 and a density of 0.905 was heat sealed to the enamel coated steel strip with the polypropylene layer in direct contact with the enamel surface using a laboratory Sentinal heat sealer. Bonding was achieved with the sealer set at 205°C, 40 pounds per square inch jaw pressure and a dwell time of 4 seconds. The heat sealed structure was then allowed to cool to ambient room temperature.

The heat sealed structure was then tested to determine the peel force required to separate the polypropylene coated aluminum foil from the enamel coated strip. The test was performed using an Amthor peel tester which applied a constant strain rate of 12 lineal inches per minute on the structure. The peel forces required to effect separation of the heat sealed layers was determined to be 3.4 pounds/inch (lbs/in).

For purposes of comparison, the procedure of Example 1 was repeated with the exception that the carboxyl modified polypropylene resin was not incorporated in the enamel coating—no measurable bond was obtained in the heat sealed structure.

EXAMPLE II

A sheet of tin-free steel was coated with an epoxy resin based enamel coating modified with Hercoprime in accordance with the procedure of Example I. Strips of the enamel coated steel were bonded together by interposing a film of polypropylene between the enamel coated surfaces and heat sealing under the conditions of Example I. The peel force required to effect separation of the heat sealed strips was determined to be 66 lbs/in.

EXAMPLE III

Hot solvent solutions of a carboxyl modified polypropylene resin were prepared by adding 0.4 parts Hercoprime A-35 (trademark) to varying amounts of oleyl alcohol to prepare resin solutions ranging in concentration from 4 to 20 percent by weight. Hercoprime A-35 is a maleic anhydride modified polypropylene resin having an inherent viscosity of about 1.7, a carboxyl content of 0.6% to 1.0%, a particle size range of 35 to 40 microns and a specific gravity of 0.9.

The oleyl alcohol-Hercoprime mixture was heated to 155°C for 15 minutes during which time the Hercoprime dissolved in the oleyl alcohol. The hot solution at 155°C was then added slowly to a rapidly stirred solution of 100 parts of an epoxy resin based enamel coating formulation composed of a 40% by weight solids consisting of 85 parts of the diglycidyl ether of Bisphenol A and 15 parts of a butylated urea formaldehyde suspended in an organic solvent mixture of approximately 25 parts xylene, 25 parts methyl isobutyl ketone, 30 parts diacetone alcohol and 20 parts butyl alcohol. To the enamel coating formulation was also added 30 parts of "Cellosolve" acetate as a diluent to adjust the flow and viscosity properties of the modified enamel formulation to that required for commercial coating specifications and 1.8 parts of a polyethylene dispersion for lubricant properties. The resultant enamel formulation had a Hercoprime concentration of 1% by weight (based on enamel solids).

The modified enamel coating formulation was applied, by means of a draw bar, to the surface of a sheet of 95 lb. tin-free steel at a dried film weight of 3.5—4.5 mg/sq. in. of steel surface.

After application of the modified enamel coating formulation, the coated sheet was baked at 370°F for 8 minutes to volatilize the solvent mixture and to cure the epoxy-urea formaldehyde-carboxyl modified polypropylene resin solids mixture to a hard enamel film.

After cooling, the tin-free steel sheet was cut into 1×4 inch strips. A closure member having a laminate structure of 3.0 to 4.0 mil aluminum foil coated with a 1.5 to 2.0 mil layer of a polypropylene resin having a melt index of 0.55 and a density of 0.90 was heat sealed to the enamel coated strips at 400°F with the polypropylene layer in contact with the enamel coated surface at a 4 second dwell time and 40 lbs/sq. in. pressure. The closure member heat sealed to the strip was allowed to cool to room temperature.

The heat sealed portion of the closure member was then tested to determine the peel force required to separate the closure member from the enamel coated strip. The peel strengths necessary for commercial acceptance generally should be in excess of 1.5 lbs/lineal inch (PLI). The test was performed using an Amthor peel tester which applied a constant strain rate of 12 lineal inches per minute on the closure member. The peel forces required to separate the closure member are summarized in Table 1 below.

For purposes of comparison, the procedure of Example III was repeated with the exception that the carboxyl modified polypropylene resin was incorporated in the enamel coating directly without first dissolving the resin in oleyl alcohol. The peel force required to separate the closure member in this comparative run is also listed in Table 1 designated by the symbol "C".

TABLE 1

Run No.	Parts Hecoprime per 100 parts Oleyl Alcohol	Parts oleyl Alc. per 100 Parts of Enamel	Peel Strength (PLI)
1	20.0	2	1.9
2	10.0	4	3.3
3	6.7	6	5.5
4	5.0	8	7.5
5	4.0	10	9.2
C	0	0	No Bond

The data in Table 1 indicates that dissolving the carboxyl modified polypropylene resin in oleyl alcohol materially improves the bond strength of the heat sealed polypropylene layer of the closure member to the enamel coated steel surface and that the more dilute the solution of the resin or the greater the amount of alcohol used to dissolve the resin, the greater is the improvement in bond strength.

EXAMPLE IV

The procedure of Example III was repeated with the exception that Alfol 1218 (trademark), a mixture of C_{12}—C_{18} aliphatic alcohols was used to dissolve the Hercoprime. Alfol 1218 has the following composition:

Alcohol	Wt.%
Dodecyl (C_{12}	40
Myristyl (C_{14})	30
Cetyl (C_{16})	20
Stearyl (C_{18})	10

Alfol 1218 solvent solutions containing Hercoprime A-35 were prepared by adding 0.34 parts Hercoprime to varying amounts of Alfol 1218 to prepare resin solutions containing varying ratios of Hercoprime and Alfol 1218. In dissolving the Hercoprime, the Alfol 1218 was heated to 100°—120°C and the Hercoprime resin powder was added. Heating was continued to 150°—160°C and the hot solution was added to 100 parts of a rapidly stirred epoxy-urea formaldehyde resin mixture (40% solids in mixed solvent solution) at room temperature. To the enamel formulation was then added 0.1 part Irganox 1010 as a 10% solution in "Cellosolve" acetate as well as additional (20 parts) "Cellosolve" acetate diluent. The resultant enamel coating formulation contained 0.8% by weight (based on enamel coating solids) Hercoprime. The peel strengths of polypropylene coated aluminum closure members heat sealed to 1x4 inch enamel coated tin-free steel strips are recorded in Table II below.

For purposes of comparison, the procedure of Example IV was repeated with the exception that the carboxyl modified polypropylene resin was incorporated in the enamel coating directly without first dissolving the resin in Alfol 1218. The peel force required to separate the closure member in this comparative run is also listed in Table II designated by the symbol "C".

TABLE II

Run No.	Parts Hercoprime per 100 parts Alfol	Parts Alfol per 100 parts Enamel	Peel Strength (PLI)
1	5.3	6	7.7
2	2.7	12	21.9
3	1.8	18	16.9
4	1.3	24	4.9
C	0	0	No Bond

The data in Table II indicates that dissolving the carboxyl modified polypropylene resin in a mixture of C_{12}—C_{18} alcohols materially improves the bond strength of the heat sealed polypropylene layer of the closure member to the enamel coated steel surface and that the strongest peel strengths are achieved when a solution containing about 2.7% by weight of the resin is used, the bond strengths diminishing as more dilute solutions are employed.

EXAMPLE V

The procedure of Example III was repeated using a variety of C_{12}—C_{22} organic alcohols and acids and C_{10} and greater hydrocarbons having boiling points above 150°C as solvents for the Hercoprime. The solvent/Hercoprime weight ratio was maintained constant at 15:1. In dissolving the Hercoprime, the solvent material and the Hercoprime powder mixture was heated to 150—160°C. The hot solution was added to the rapidly stirred epoxy-urea formaldehyde enamel at room temperature. To the enamel formulation was then added an Irganox 1010 as a 10% solution in "Cellosolve" acetate as well as additional "Cellosolve" acetate diluent. The resultant enamel coating formulation contained 1% by weight (based on enamel coating solids) Hercoprime and had the following composition:

	Grams	Solids Content (grams)
Epoxy-urea/formaldehyde suspension	100.0	40
Hercoprime	0.4	0.4
Solvent for Hercoprime	6.0	0
Irganox 1010	1.0	0.1
Cellosolve acetate diluent	25.0	0

The peel strengths of polypropylene coated aluminum closure members heat sealed to 1×4 inch enamel coated tin-free steel strips are recorded in Table III below, the enamel coatings having Hercoprime incorporated therein using different solvents within the scope of the appended claims.

For purposes of comparison, the procedure of Example V was repeated with the exception that the Hercoprime resin was incorporated in the enamel coating formulation dissolved in a solvent which is other than a saturated or olefinically unsaturated aliphatic acid, an alcohol having 10 to 22 carbon atoms, or a saturated or unsaturated hydrocarbon having 10 to 30 carbon atoms. The peel forces required to separate the closure member heat sealed to these comparative enamel coatings are also listed in Table III. These comparative tests are designated by the symbol "C".

TABLE III

Run No.	Solvent	Chemical Type	Temperature at which Hercoprime Resin dissolves (°C)	Peel Strength (PLI)
1	Oleyl alcohol	C_{18} Olefinic alcohol	120	48.0
2	Alfol 1218	C_{12}—C_{18} Aliphatic alcohol mixture	120	10.5
3	Cetyl alcohol	C_{16} Aliphatic alcohol	120	8.2
4	Stearyl alcohol	C_{18} Aliphatic alcohol	120	5.1
5	Tridecyl alcohol	C_{13} Aliphatic alcohol	120	3.5
6	Arachidyl alcohol	C_{20} Aliphatic alcohol	120	2.2
7	Dodecyl alcohol	C_{12} Aliphatic alcohol	120	1.9
8	Isostearic Acid	C_{18} Aliphatic Acid	130	2.9
9	Oleic acid	C_{18} Unsaturated carboxylic acid	125	2.4
10	Marine fatty acid	C_{14}—C_{22} Fatty acid mixture	120	2.2
11	Mineral oil	C_{20}—C_{26} Aliphatic carbons	120	10.0
12	Kerosene	C_{10}—C_{16} Aliphatic hydrocarbon	135	5.1
13	Chevron Alpha Olefins	C_{11}—C_{15} Olefin hydrocarbon mixture	120	4.0
14	1-Dodecene	C_{12} Unsaturated hydrocarbon	115	1.1
C_1	Ethyl hexyl alcohol	C_8 Aliphatic alcohol	125	0
C_2	Butyl alcohol	C_4 Aliphatic alcohol	Resin insoluble at boiling point	—
C_3	Isopropanol	C_3 Aliphatic alcohol	Resin insoluble at boiling point	—
C_4	Diacetone alcohol	Aliphatic ketoalcohol	Resin insoluble at boiling point	—
C_5	Butyl cellosolve	Aliphatic glycolether	Resin partly soluble at 160°C	—
C_6	Xylene	Aromatic hydrocarbon	110°C	0
C_7	1,2,3,4-Tetrahydro naphthalene (tetralin)	Aromatic hydrocarbon	90°C	0

TABLE III (cont.)

C_8	Diisobutyl ketone	Aliphatic ketone	Resin insoluble at boiling point	—
C_9	Hydroxy ethyl azeliate	β-Hydroxy ethyl fatty acid ester	Resin insoluble at 150—160°C	—
C_{10}	Glyceryl monooleate	C_{18} Olefinic ester	Resin insoluble	—

The data in Table III shows Hercoprime when added to an enamel coating formulation dissolved in C_{12}—C_{20} aliphatic alcohols and acids and C_{10} or more aliphatic hydrocarbons results in enamel surfaces to which polypropylene may be heat sealed. Although Hercoprime is soluble in hot xylene, tetralin and ethyl hexyl alcohol, the enamel coatings, which were prepared using these hot solutions, did not form any heat seal bonds with polypropylene surfaces. Lower aliphatic alcohols such as butanol and isopropanol and other solvent materials such as butyl cellosolve, diacetone alcohol and methyl isobutyl ketone could not be used to incorporate Hercoprime in enamel coating formulations as Hercoprime is not soluble in these common organic solvents at their boiling points.

EXAMPLE VI

The procedure of Example V was repeated with the exception that the heat sealed structure was baked at 400°F for 15 seconds to simulate conditions encountered during manufacture of metal container ends. The results of these tests are recorded in Table IV below.

TABLE IV

Run No.	Percent Hercoprime Based on Enamel Solids	Hercoprime Solvent	Peel Strenths (PLI) Before Bake	After Bake
1	0.6	Oleyl alcohol	9.5	11.5
2	0.9	Oleyl alcohol	26.1	39.0
3	0.8	C_{12}—C_{18} Aliphatic* alcohol blend	1.4	3.4
4	1.0	Stearyl alcohol	5.1	7.3

*Alfol 1218

The results in Table IV show that the bond strength of a polypropylene layer heat sealed to an enamel coating modified in accordance with the method of the present invention increases if the structure receives additional heating.

EXAMPLE VII

The procedure of Example V was repeated to modify enamel coating formulations with oleyl alcohol solutions of Hercoprime A-35 with the exception that the temperature of the Hercoprime solution at the time of its addition to the enamel coating formulation was varied from 23°C to 155°C. The peel strengths of polypropylene coated aluminum closure members heat sealed to 1×4 tin-free steel strips coated with the enamel coating formulations are recorded in Table V.

TABLE V

Temperatures at which Hercoprime solution added to enamel	Peel Strengths (PLI)	Comments
155°C	48	solution
100°C	6.1	Gel
23°C	6.4	Gel

The results recorded in Table V indicate that superior bonding results are obtained with enamels modified with Hercoprime solutions heated to temperatures above 100°C at their time of addition to the enamel formulation. If the Hercoprime solution is cooled to temperatures of 100°C or less at time of addition to the enamel formulation, the Hercoprime crystallizes out as gel which materially affects the bonding results with the enamel.

EXAMPLE VIII

The procedure of Example V was repeated with the exception that Hercoprime G-35 was substituted for Hercoprime A-35. Hercoprime G-35 differs from Hercoprime A-35 in that Hercoprime G-35 has carboxyl content of 3.0 to 4.0% and has a lower inherent viscosity. In dissolving Hercoprime G-35 in oleyl alcohol, the alcohol was heated to 120°—130°C and the Hercoprime powder added. Heating was continued to 150°—160°C and the hot solution added to the rapidly stirred epoxy-urea formaldehyde enamel at room temperature. To the enamel formulation was then added Irganox 1010 as well as "Cellosolve" acetate diluent. The resultant enamel coating formulation contained 0.5—1% by weight (based on enamel coating solids) Hercoprime G-35 and had the following composition:

	Grams	Solids Content (Grams)
Epoxy-urea/formaldehyde suspension	100.0	40
Hercoprime G-35	0.2—0.4	0.2—0.4
Oleyl alcohol	6.0	0
Irganox 1010	1.0	0.1
Cellosolve acetate diluent	25.0	0

The peel strengths of polypropylene coated aluminum closure members heat sealed to 1x4 inch enamel coated tin-free steel strips are recorded in Table VI.

TABLE VI

% Hercoprime G-35 Added to Enamel	Peel Strength (PLI)
1.0	42
0.5	45

The words "Irganox" and "Cellosolve" used in this specification are registered Trade Marks.

The use of the enamel coating composition of the present invention in a method of bonding a propylene polymer to a metal surface is described in our British Patent Specification No. 1565697 [Application No. 37898/76].

WHAT WE CLAIM IS:—

1. An enamel coating composition comprising a carboxyl modified polypropylene resin incorporated into an epoxy resin enamel coating formulation containing a heat-activatable aminoplast cross-linking resin.

2. A coating composition according to Claim 1, wherein the aminoplast cross-linking resin is a urea-formaldehyde resin.

3. A coating composition according to Claim 2, wherein the solids content of the composition comprises 60 to 95% by weight of the epoxy resin, 5 to 40% by weight of the urea-formaldehyde resin, and 0.01 to 5% by weight of the carboxyl modified polypropylene resin.

4. A coating composition according to Claim 3, wherein the said solids content comprises 70 to 90% of the epoxy resin, 5 to 25% by weight of the urea-formaldehyde resin and 0.1 to 5% by weight of the carboxyl modified polypropylene resin.

5. A coating composition according to any one of the preceding claims, wherein the carboxyl modified polypropylene resin is the reaction product of polypropylene and an unsaturated dicarboxylic acid or anhydride and contains 0.1% to 5.0% by weight carboxyl groups.

6. A coating composition according to Claim 5, wherein the unsaturated anhydride is maleic anhydride.

7. A coating composition according to any one of the preceding claims, wherein the enamel coating composition is one which has been prepared by dissolving the carboxyl modified polypropylene resin in a solvent heated to a temperature greater than 100°C to form a solution thereof, the solvent being a saturated or olefinically unsaturated aliphatic acid, an alcohol having 10 to 22 carbon atoms or a saturated or unsaturated hydrocarbon having 10 to 30 carbon atoms, or a mixture thereof, and adding the resultant resin solution to the enamel coating formulation comprising the epoxy resin and the urea formaldehyde resin.

8. A coating composition according to Claim 7, wherein the resin solution is at a temperature greater than 100°C when added to the enamel coating formulation.

9. A coating composition according to Claim 7 or 8, wherein the solvent is oleyl alcohol.

10. A coating composition according to Claim 7 or 8, wherein the solvent is dodecyl alcohol.

11. A coating composition according to Claim 7 or 8, wherein the solvent is myristyl alcohol.

12. A coating composition according to Claim 7 or 8, wherein the solvent is cetyl alcohol.

13. A coating composition according to Claim 7 or 8, wherein the solvent is stearyl alcohol.

14. A coating composition according to Claim 7 or 8, wherein the solvent is tridecyl alcohol.

15. A coating composition according to Claim 7 or 8, wherein the solvent is arachidyl alcohol.

16. A coating composition according to Claim 7 or 8, wherein the solvent is oleic acid.

17. A coating composition according to Claim 7 or 8, wherein the solvent is isostearic acid.

18. A coating composition according to Claim 7 or 8, wherein the solvent is mineral oil.

19. A coating composition according to Claim 7 or 8, wherein the solvent is kerosene.

20. A coating composition according to Claim 7 or 8, wherein the solvent is 1-dodecane.

21. A coating composition according to Claim 7 or 8, wherein the solvent is a mixture of C_{11}—C_{15} olefinically unsaturated hydrocarbons.

22. A coating composition according to Claim 1 substantially as described in the foregoing Example I or Example II.

23. A coating composition according to Claim 1 substantially as described in any one of the foregoing Examples III to VIII.

24. A metal surface coated with an enamel coating formed from an enamel coating composition as claimed in any one of the preceding claims.

PAGE, WHITE & FARRER,
Chartered Patent Agents,
27 Chancery Lane,
London, WC2A 1NT.
Agents for the Applicants.

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.

1565698 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

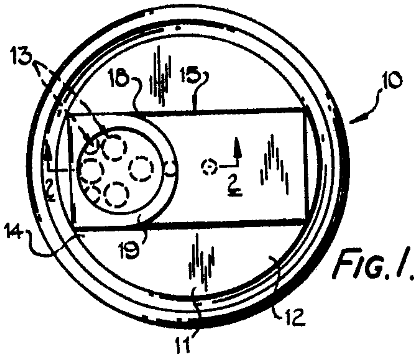


FIG. 1.

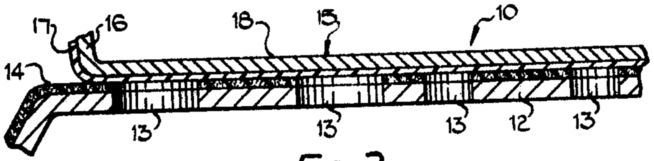


FIG. 2.

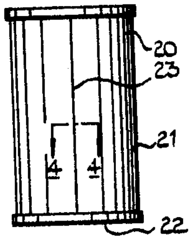


FIG. 3.

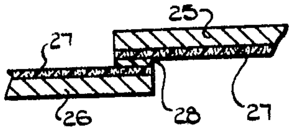


FIG. 4.