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COATING

This invention relates to a PVC-free coating for metal containers. More particularly, it relates to PVC-free coatings for deep draw container forming.

Metal containers for receiving foods generally have a coating to prevent contact between the filled product and the metal, so that there is no disadvantageous influence on the quality of said product and so as to prevent corrosion to the metal by said product. For producing containers of this type, such as tin cans, use is made of metal sheets which, prior to their deformation or shaping, are provided with a suitable coating. Known epoxy-phenolic lacquers are suitable for this purpose and as a result of their colour tone they are also referred to as gold lacquers. Of late and in particular in conjunction with modern processing and deformation processes (cf. below) more and more PVC-based organosols have been used.

Of the various processing and deformation processes which can be used, within the scope of the present invention particular interest is attached to deep drawing and more especially multi-stage DRD deep drawing (draw and redraw). These processing and deformation processes make increased demands on the sheet metal coating, i.e. the coating must not only be as free as possible from pores and cracks and adhere well, but must also have a good drawing property or capacity, so that the afore-mentioned characteristics are also present following deep drawing. Whereas for the production of three-part tin cans, use is made of sheet metal thicknesses of approximately 0.19 to 0.25 mm, for DRD deep drawing, harder, but thinner metal sheets with a thickness of 0.18 mm and less are used. A suitable material is e.g. tin plate. However, preference is given to metal sheets, which are given an extremely thin chromium surface coating.

PVC-based organosols are suitable for the coating of metal sheets, which are to be shaped or deformed in accordance with the afore-mentioned deep drawing processes. The organosol is applied prior to the deformation of the sheet (normally after a roll coating process) and is then normally baked for 8 to 15 minutes at approximately 175°C to 225°C. For this purpose the metal sheet is generally passed through a drying tunnel. In the case of two-sided sheet metal coating, the organosol is firstly applied to one side of the sheet and then baked and subsequently the other side of the sheet is treated in the same way. As a function of the intended use, the coating thicknesses are between 7 and 30 g (dry weight) per m². It is important that the coating adheres well, has no pores and cracks and is mechanically stable, so that a coating is obtained which is resistant to corrosion and sterilization and which is not sensitive to mechanical stresses.

Although PVC-based organosols lead to coatings which largely meet the demands of deep drawing processes, there is a considerable need for further improvements to the coating characteristics, i.e. in particular for a further reduction to the porosity and an improvement to the stability with respect to more or less aggressive filled products. Reference is also made in this connection to the prevention of the diffusing of the plasticizer into the filled material. An important disadvantage of coatings based on PVC-containing organosols is that the PVC absorbs colourings like the pink colouring of the shrimps and crabs, so that when emptying a can filled with such a product, an unattractive pink staining can be seen on the internal coating which, although admittedly not impairing the product quality, is certainly an irritant to the user.

Moreover, the use of vinyl chloride containing materials has fallen into disfavor. Vinyl chloride materials are difficult to produce, are corrosive in nature and are difficult to recycle. Several countries, especially in Europe are limiting the use of such materials in containers, especially food containers due to the environmental and health problems associated with vinyl chloride based products.

Another possibility for the coating of metals for the production of receptacles such as tin cans, tubes and sheet metal containers of all types is the afore-mentioned use of epoxy-phenolic coatings, which are applied to the sheet metal in the same way as the afore-mentioned organosols and are then baked for 8 to 15 minutes at approximately 175° to 225°C. Such coatings typically contain from 75-95% epoxy with the remainder being a phenolic resin. The resulting coatings have excellent characteristics and in particular a very good chemical stability and therefore resistance to the action of aggressive filled products. However, these coatings suffer from the disadvantage that resistance to aggressive filled products is not combined with adequate elasticity and that therefore they are not drawable and consequently cannot be used for deep drawing processes and especially DRD deep drawings processes.

As such, these epoxy-phenolic coating are typically applied after formation of the container, which is expensive and time consuming.

The present invention seeks to further improve coatings and in particular interior coatings of metal containers for receiving foods and to avoid the afore-mentioned disadvantages of known coatings, especially those based upon PVC.

A PVC-free coating composition is provided which is suitable for coating an inner-surface of a metal container which composition comprises a crosslinkable phenoxy resin or a blend of crosslinkable phenoxy resins, dissolved or
5 dispersed in a solvent or diluent, and a second resin which is a epoxy or phenolic resin or a blend thereof dissolved or dispersed in a solvent or diluent and a hardener for the phenoxy resin, which composition is capable of withstanding a deep drawing process. Preferably, the coating
10 composition also contains pigments, viscosity modifiers, etc.

Also provided is a metal container comprising a metal substrate having an inner surface and an outer surface and a PVC-free coating on at least the inner surface, which
15 coating has been formed using a composition as hereinbefore defined.

The present invention further provides a metal sheet suitable for use in the formation of a deep drawn two piece container comprising a metal substrate having a first and a
20 second surface, and wherein at least the first surface is coated by a PVC-free coating, ^{which coating has been formed using a composition} ~~comprised of a phenoxy resin and second resin~~ as hereinbefore defined.

The invention yet further provides a process for producing a metal container, which comprises coating a
25 metal substrate with a PVC-free coating composition of the invention.

As a result of the inadequate elasticity of epoxy-phenolic coatings, the phenoxy-epoxy coating would not be expected to be appropriate for metal coatings. However, it
30 has surprisingly been found that the elasticity behaviour of the phenoxy-epoxy coatings is improved to such an extent that the coating is able to withstand the stresses of the deep drawing process, particularly the DRD deep drawing process, i.e. the thus produced coatings have an extremely
35 low porosity combined with an optimum chemical stability.

Another advantage of the inventive coating is that the PVC-based organosol is no longer used, eliminating the

concerns of recycling and disposing of vinyl chloride containing products.

Phenoxy resins are well known to those skilled in the art. Phenoxy resins are typically a high molecular weight thermoplastic copolymer of bisphenol A and epichlorohydrin and has a basic molecular structure of:



wherein n has a value from about 50 to about 200.

While the resin uses the same raw materials as epoxy resins, it is different in that it contains no epoxy groups. Rather, it is cured or crosslinked by the reaction of a hardener (crosslinking agent) with its hydroxyl groups.

As the phenoxy resins are of high molecular weight, they tend to be very viscous. The present invention uses a second resin which is an epoxy or phenolic resin and diluent or solvent for phenoxy and the second resin to obtain the desired viscosity and solids content suitable for container coatings. Blends of one or more different phenoxy resins and/or one or more second resins may also be used to achieve the desired results.

The ratio of phenoxy resins to second resin (by weight, solids) is generally from 99:1 to 25:75, depending upon the molecular weight of the components selected, the use of a diluent or solvent and the desired viscosity/solids content that one wishes to achieve.

It is preferred that the ratio (by weight, solids) of phenoxy resin to the second resin be at least 50:50, more preferably 65:35 regardless of whether one or more of each type of resin is used.

Suitable phenoxy resins include but are not limited to BAKELITE* PKHH resins available from Union Carbide, or DER* XZ87720 resins from Dow.

* Registered Trade Marks.

Suitable epoxies include but are not limited to DER 668 resins, available from Dow or ARALDITE* resins, available from Ciba Geigy, or EPON or EPONOL epoxy resins from Shell Chemical Company or EPOTUF* resins from
5 Reichhold Chemicals, Inc.

Other second resins which may be used include, for example, a phenolic resin known as PHENODUR* from Hoechst.

Suitable diluents or solvents for the phenoxy and second resin include but are not limited to ketones,
10 esters, ethers, such as glycoethers, alcohols, hydrocarbons, especially aromatic hydrocarbons or a mixture thereof. Selection of the diluents/solvents depends upon the viscosity of the resin blend without a diluent or solvent and the desired viscosity and solids content of the
15 coating composition. Preferably, the diluents/solvents used are compatible with each other and provide adequate dispersion/dissolution of the components in the coating composition.

If desired, the phenoxy resin and/or the second
20 resin, if amenable to doing so, may be subject to a precondensation step to improve their compatibility and reduce porosity. This is typically accomplished by mixing the resin or resins with a suitable solvent/diluent and a catalyst, such as an acid catalyst and allowing the
25 resin(s) to partially react or prepolymerize before use. In doing so, however one needs to ensure that the solids content of the coating is kept within the desired range and that the other desired characteristics

* Registered Trade Marks

of the coating are not adversely affected.

Cross linkers or hardeners for the phenoxy and/or second resin, may for example be amines, urea-formaldehyde resins, or anhydrides.

- 5 Further conventional components of the coating are additives such as lubricants e.g. lanolin, polyethylene wax and other waxes; catalysts such as acid catalysts; pigments or fillers (e.g. aluminium; iron oxide or carbon black), stabilizers, dyes, and other processing aids.

The quantitative proportions of said components are dependent on the desired processing characteristics of the coating composition and the desired characteristics of the baked coating. Suitable quantity ranges and other details in connection with the aforementioned components are well known to those skilled in the art and appear in the prior art, e.g. in European patent application 254 755.

The coating applied to the metal sheet is generally baked for 8 to 15 minutes at 175° to 225°C and preferably for about 10 minutes at 180° to 200°C.

The thickness of the coating is generally in the conventional range between 7 and 30g (dry weight) per m² and is preferably 10 to 15 g/m².

The sheet metal side subsequently forming the container outside should also be coated for technical reasons of processing. For this purpose an organosol or epoxy-phenolic coating can be used. If desired, the sheet metal side subsequently forming the container outside can be provided with a coating of the invention in the above described way. The application of the coating to the sheet metal side subsequently forming the container outside usually takes place in a process step preceding the coating step of the sheet metal side subsequently forming the container inside. However, it can also take place at the same time or at an intermediate or subsequent process step depending upon the production facilities.

The coated sheet metal is then shaped to the desired container. This shaping preferable takes place by deep drawing and especially by DRD deep drawing, preference being given to chrome plated (see above) or tin-plated metal sheets. These are so-called ECCS (electrolytical chromium coated steel) or ETP (electrolytical tin plate) metal sheets.

EXAMPLE

Conventional tin plate and ECCS metal sheets were coated with the following coatings:

COMPARATIVE EXAMPLE

By mixing the stated ingredients a typical organosol for DRD drawing was prepared:

Vinylchloride	
homopolymerisate	29.20 wt. %
Vinylchloride	
copolymerisate	6.80 wt. %
Phenolic resin	3.20 wt. %
Epoxy resin	3.40 wt. %
Acrylate resin	6.80 wt. %
Aluminium pigment	5.00 wt. %
Tin octoate Catalyst	0.02 wt. %
Lanolin Lubricant	1.00 wt. %
Diluent blend	<u>44.58 wt. %</u>
of Aromatic hydrocarbons	
alcohols and ketones	
	100.00 wt. %

EXAMPLE 1

By dissolving and mixing of the stated ingredients an phenoxy-epoxy coating was prepared.

50 parts by weight (solids) of a phenoxy resin (BAKELITE PKHH from Union Carbide);

50 parts by weight (solids) of a blend of one or more epoxy resins and phenolic resins;

5 parts by weight (solids) of aluminium pigment; and
1 part by weight of lanolin.

Sufficient solvent/diluent to obtain a coating composition of 45% solids (by weight).

Cans drawn from the so coated metal sheets were subjected to the following tests:

(A) Porosity Test

Electrolytical conductivity after filling the cans to be tested with a suitable electrolyte is considered to be a measure for lacquer quality. The indication on the test apparatus was in mA.

(B) Sterilisation Test

Formed cans are placed into a sterilizer at a temperature of 121°C for 30 minutes in the presence of water and then withdrawn and observed.

Water absorption and blister formation were evaluated.

The results obtained are summarized in the following table.

TABLE I

COATING CHARACTERISTICS

Coatings were of a thickness from 10 to 15 g/m².

TEST

	<u>PVC</u>	<u>INVENTION</u>
(A) Porosity	1mA	1-2 mA
(B) Sterilisation	good	excellent

Cans produced according to the process of the invention when compared with those having known PVC organosol coatings gave very satisfactory results in the porosity test and in sterilization tests (30 minutes; 121°C.) in water, and in all aspects of the tests carried out the coatings of the present invention were at least as good, but usually better than the known PVC coatings.

While the present invention has been described in relation to the preferred embodiments, other embodiments can achieve the same results.



CLAIMS

1. A PVC-free coating composition suitable for coating an inner surface of a metal container for receiving food which composition comprises a crosslinkable phenoxy resin or a blend of crosslinkable phenoxy resins, dissolved or dispersed in a solvent or diluent, and a second resin which is an epoxy or phenolic resin or a blend thereof dissolved or dispersed in a solvent or diluent and a hardener for the phenoxy resin, which composition is capable of withstanding a deep drawing process.
2. A composition according to claim 1 wherein the second resin is an epoxy resin.
3. A composition according to claim 1 or 2 wherein the solid ratio, by weight, of phenoxy to second resin is from 99:1 to 25:75.
4. A composition according to claim 3 wherein the proportion of phenoxy resin is at least 50:50.
5. A composition according to any one of the preceding claims wherein the phenoxy and second resin are dissolved in a solvent which is a hydrocarbon, ether or ester.
6. A composition according to any one of the preceding claims further comprising an aluminium pigment, a hardener for the phenoxy resin which is an amine, urea-formaldehyde resin or anhydride or a lubricant.
7. A metal container comprising a metal substrate having an inner surface and an outer surface and a PVC-free coating on at least the inner surface, which coating has been formed using a coating composition as defined in any one of claims 1 to 6.
8. A container according to claim 7 wherein the coating is capable of withstanding sterilisation at 121°C for 30 minutes in water.
9. A metal sheet suitable for use in the formation of a deep drawn two piece container comprising a metal substrate having a first and a second surface, and wherein at least the first surface is coated by a PVC-free coating,



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which coating has been formed using a composition
~~comprised of a phenoxy resin and a second resin~~ as defined
in any one of claims 1 to 76.

10. A process for producing a metal container which
comprises coating a metal substrate with a PVC-free coating
5 composition as claimed in any one of claims 1 to 76.

11. A process according to claim 10 wherein after
the coating, the metal container is formed from the metal
substrate so that an inner surface of the container is
coated.

10 12. A process according to claim 11 wherein the
metal container is formed by a draw redraw deep drawing
process.

15 13. In a metal container suitable for containing
food formed by a draw redraw deep drawing process and
having a coating formed on an inner surface of the
container, the improvement comprising a PVC-free coating
formed from a composition comprising a crosslinkable
phenoxy resin or a blend of crosslinkable phenoxy resins
dissolved or dispersed in a solvent or diluent and a second
20 resin which is an epoxy or phenolic resin or a blend
thereof dissolved or dispersed in a solvent or diluent and
a hardener for the phenoxy resin and wherein the coating is
applied to the inner surface of the container prior to the
draw redraw deep drawing process.