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FERROUS METAL ICE TRAY

Albert L. Bunting, Dearborn, and Arthur C. Schultz, Detroit, Mich.; said Schultz assignor to said Bunting

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The present invention relates to a novel ferrous metal ice tray having an improved corrosion-resistant ornamental and protective coating.

Metallic trays and grids customarily used in refrigerators for producing ice cubes or other frozen substances are subjected in use to a wide variation in temperature and are used under conditions particularly conducive to surface corrosion. Such objects frequently are subjected to elevated temperatures on the exterior surfaces while ice or other frozen materials are in the pan. Also, such pans may be used for cooking or baking and are subjected to considerable handling. The surfaces thereof also are subjected to much wear and abrasion, particularly when used with grids adapted to free the frozen material therefrom by mechanically applied forces.

Prior to the present invention, copper, aluminum or other non-ferrous metals or alloys were considered to be the principal metals satisfactory for use in connection with such objects since these metals do not rust or corrode under the conditions of use. Since the materials frozen or prepared in such objects normally comprise food or other substances intended for human consumption, it is essential that any coating applied thereto must be non-toxic in character, and be free from materials which taint or impair the taste of the food frozen or prepared therein.

Protective coatings suggested heretofore for use with steel or other ferrous metal objects have been defective in one or more of the foregoing respects and therefore have been unsatisfactory for use with steel or ferrous metal ice trays or grids.

Accordingly, it is one object of the present invention to provide a coating for a steel or ferrous metal ice tray or grid which fulfills the aforesaid requirements for such a coating, and which therefore effectively and satisfactorily protects the tray and grid from rusting or corrosion despite the wide temperature ranges to which these articles are normally subjected, and despite the handling, wear and abrasion to which they are also normally subjected.

Another object of this invention is to provide a protective coating for steel or ferrous metal ice trays or grids which is not toxic, and which is free of materials which taint or impair the taste of the materials which are prepared or frozen in the tray.

Another object of the invention is to provide a protective coating which may be used with rubber or the like without reacting therewith or pro-

ducing other deleterious effects, thus permitting a rubber grid or insert to be safely and satisfactorily employed in connection with a steel or ferrous metal tray, if desired.

A further object of the invention is to provide a coating for an ice tray or grid to which frozen materials, such as ice, do not adhere very firmly, and thus to provide a tray and grid from which ice cubes or the like may be readily removed.

Still a further object of the invention is to provide a protective coating on an ice tray which consists of a hard, tough, relatively flexible film or layer which fills irregularities in the metal surfaces to produce a smooth surfaced product, such coating being pleasing in appearance and being white or colored as desired.

Other objects and advantages of this invention will appear in the following description and appended claims. Before explaining in detail the present invention it is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation, and it is not intended to limit the invention beyond the requirements of the prior art.

In order to apply the present protective coating to ferrous metal objects, it is desirable to clean the surfaces to be coated.

For example, steel refrigerator ice trays are normally fabricated from a sheet of steel by drawing or stamping operations. Accordingly, said trays usually possess oil on their surfaces, as well as dirt and other foreign substances. To clean these surfaces we prefer to use an emulsion type cleaner such a triethanol amine soaps. The latter comprise triethanol amine as an emulsifying agent, water, and a suitable fat or oil containing fatty acids, such as oleic acid, stearic acid or the like. By way of still further example, other emulsion type cleaning agents include kerosene and water which may be emulsified by a suitable emulsifying agent, triethanol amine also being suitable to form this emulsion.

It will be understood, however, that other cleaners may be used including solvents for the oil or grease normally found on the surfaces of the aforesaid objects. Among such solvents are benzene, naphtha, gasoline or mixtures thereof, stabilized trichlorethylene, carbon tetrachloride, and perchlorethylene.

In connection with the cleaning operation, it is also recommended that the water used to form the emulsion be carefully checked for hardness and, in general, be checked for impurities contained therein. If necessary, this water should be conditioned, that is, it should be softened or

treated to remove impurities, if deleterious, or treated to render said impurities harmless. We have found it is preferable that the water should have a pH value of approximately 8. The pH value may be varied in many waters by the use of relatively small amounts of sodium metasilicate, sodium phosphate and with phosphoric acid. It will be understood that water softening or conditioning is well understood by chemists familiar with this subject and that one skilled in the art may take suitable steps to provide the proper water to insure an effective emulsion type cleaner. It will also be understood that this emulsion type cleaner may be utilized in any of the various ways, that is, the object to be cleaned may be submerged in the cleaner, sprayed therewith, etc., preferably at elevated temperatures such as approximately 160° F. to approximately 180° F.

After the objects have been subjected to the cleaning operation, we have found it desirable to rinse them in order to remove the cleaning solution from the surfaces. For this rinsing operation we have found that hot water is effective. Also after the cleaning and rinsing operation, it is desirable to dry the surfaces of the object by any suitable means, such as a stream of air under pressure, dry steam, heat or the like.

In order to properly protectively coat ferrous metal objects according to the present method, it is desirable that the surfaces to be coated not only be clean but that they be freed from prominent burrs or other irregularities which normally are produced by stamping or drawing operations. For the purpose of providing this desired surface a sand blasting operation may be employed. For this purpose any conventional and suitable sand blasting apparatus or device may be utilized. Sand itself may be employed as the medium therein as well as steel shot or other substances normally employed in sand blasting operations.

After the sand blasting operation it is, of course, desirable that the surfaces be subjected to a further cleaning operation in order to remove sand or other materials which may be present on the surfaces as a result of the sand blasting operation, or as a result of the handling operations necessary for carrying out said operation. Any suitable cleaning operation may be utilized for those purposes, such for instance as one of the emulsion type cleaners described in detail hereinbefore.

According to the present invention at least two coatings or layers are disposed upon the surfaces of the ferrous metal ice tray to be protected. The first or innermost of these layers is referred to herein as the "sub-coating." This "sub-coating" is produced by immersing the article in heated dilute solutions of phosphoric acid or phosphates, or submerging it in similar solutions of chromates or chromic acid to produce an adherent coating on the surface consisting of iron phosphates or chromates. Processes of this general character are known and are practiced under a number of names, such as "Bonderizing," "Granidizing" and the "Chromadine" process. The latter process may be carried out by immersing the ferrous metal object to be coated in a bath or solution containing chromic acid and sodium chloride. The former processes are fully explained in several United States Letters Patent among which are the following, reference to which is hereby made: Green et al. No. 1,651,694, Tanner and Darsey No. 1,888,189, and Tanner and Lodeesen No. 1,911,726. As a result

of carrying out the foregoing sub-coating operation, the refrigerator tray, or other ferrous metal object treated, will be provided with a rust resistant coating consisting essentially of ferrous phosphates or chromates which cover the surfaces of the object. However, this coating is not sufficient in itself to protect the object from rusting or corrosion when it is subjected to handling, abrasion, wear and relatively great temperature changes to which a refrigerator tray, for instance, is subjected. Accordingly, in practicing the present invention an additional coating is provided over the sub-coating.

Prior to applying this additional coating or layer the article bearing the sub-coating is first washed, as in hot water. In addition, it may be immersed for relatively short times in a solution of chromic acid, particularly if chromic acid is not utilized in the sub-coating operation. If the article bearing the sub-coating is placed in the chromic acid solution, as recommended, it is thereafter dried as by a blast of hot air, steam, heat, compressed air or the like.

The ferrous metal object bearing the sub-coating is next provided with a protective coating consisting of a novel and improved resinous material. As more fully explained hereinafter, the coating comprises polymerized or reacted alkyd resins, urea formaldehyde resins and melamine formaldehyde resins together with pigments. Furthermore, we have found it desirable to utilize at least two layers of this resinous material which, for present purposes, we refer to as the "prime" coating and the "finish" coating.

In order to apply the present resinous coatings there is prepared a coating bath or solution containing the resinous materials in their unreacted or in their partially reacted or partially polymerized or unpolymerized form, plus pigments and solvents. This bath or solution is then applied to the object as by dipping or spraying and is thereafter adhered to the object by air drying and also by baking as explained more fully hereinafter.

GENERAL FORMULA OF COATING BATH OR SOLUTION

TO MAKE 100 GALLONS

Pigments

	Pounds
Titanium dioxide.....	Approximately 250 to 350
Inert pigments.....	Approximately 50 to 150
Pigment extender.....	Approximately 35 to 100

Resins

	Pounds
Alkyd resins.....	Approximately 60 to 120
Urea formaldehyde resins.....	Approximately 12 to 100
Melamine formaldehyde resins.....	Approximately 20 to 120

Solvents

	Pounds
Benzol.....	Approximately 100 to 400
Xylol.....	Approximately 100 to 400
Butanol.....	Approximately 1 to 20
Hexyl alcohol.....	Approximately 5 to 15
Mineral spirits.....	Approximately 0 to 100

The aforesaid ingredients may be varied within the above ranges provided, however, that the

total solids (pigments plus resins) should not exceed approximately 80% of the entire weight of the bath or solution and should not be less than approximately 60% by weight thereof. As a practical matter this means that the total weight of all of the solvents combined should not greatly exceed 400 pounds.

Referring to specific substances which may be utilized as the above ingredients and to equivalents therefor, we have found that one of the pigments should be titanium dioxide or zinc sulphide. The inert pigments referred to above may be any suitable pigments adapted to serve as a filler or binder, and many such pigments will occur to one skilled in the art. Among them are barium sulfate and silica. The pigment extender referred to above is utilized principally to prevent separation of the other pigments from the solution or bath, and to keep the entire pigment content in a finely divided and suspended condition. We recommend for this purpose the use of calcium carbonate and particularly that form of calcium carbonate referred to in the art as "Multiflex." This is a specially precipitated type of calcium carbonate bearing an electrical charge in solution.

Referring now to the resins mentioned in the above general formula, the urea formaldehyde resin and melamine formaldehyde resin are specific types of resins and therefore require no further explanation. The alkyd resins, of course, cover a relatively wide class of resins and we have found that numerous members of this class of resins may be employed. We particularly recommend, however, the use of a glycerol phthalate type of alkyd resin modified by a drying oil or a non-drying oil. In particular, we recommend as a drying oil modified glycerol phthalate resin, that a glycerol phthalate resin reacted with coconut oil be employed. In addition, we recommend that the formaldehyde resins (the urea formaldehyde plus the melamine formaldehyde resins) should be used in proportions such that not less than approximately 30 parts by weight of the total resin content are formaldehyde resins. The formaldehyde resins also may be used in amounts greater than approximately 30 parts by weight of the total resin content. We believe that the alkyd resins function as plasticizers for the formaldehyde resins; but whatever the explanation, the use of both of these types of resins appears to be of importance in securing our improved protective coating.

Referring to the solvents mentioned in the above general formula, almost any combination of the particular solvents mentioned above can be utilized provided that the cyclic type of organic solvents predominates. Examples of such cyclic type of organic solvents in the above general formula are benzol and xylol. Turpentine is another cyclic type of solvent which may be used. As indicated by this general formula, these cyclic type compounds may be diluted by or mixed with other types of compounds, such as the alcohols or mineral spirits mentioned. Other suitable organic solvents may be employed for this diluting or mixing process, if desired. We have found that the undiluted cyclic type of solvents are satisfactory, but a mixing or dilution of the character mentioned is desirable as a practical matter since the cyclic type of compounds are not only relatively expensive, but if used without dilution or mixing they tend to produce obnoxious fumes.

By way of further explanation but not of limi-

tation, one specific formula utilized for compounding the present coating solution or bath is as follows:

SPECIFIC COATING SOLUTION OR BATH

<i>Pigments</i>		Pounds
Titanium dioxide ("Rutile" type—freshly precipitated)	-----	260
Barium sulfate	-----	138
Calcium carbonate (Multiflex type)	-----	77
<i>Resins</i>		Pounds
Drying oil modified glycerol phthalate resins	-----	160
Non-drying oil modified glycerol phthalate resins	-----	108
Urea formaldehyde resins	-----	13
Melamine formaldehyde resins	-----	48
<i>Solvents</i>		Pounds
Benzol	-----	145
Xylol	-----	123
Butanol	-----	20
Hexyl alcohol	-----	13
Mineral spirits	-----	97

While a suitable coating solution or bath made up in accordance with the foregoing disclosure may be utilized for either the prime or finish coating, we have found that certain changes for the finish coating appear to be desirable. In the finish coating solution it is desirable to decrease the proportion of inert pigments as compared with the proportion of such pigments contained in the prime coating solution. Also, the total pigment content of the finish coating solution should preferably be in the lower range of proportions given in the above general formula and should be less than the total pigment content in the prime coating solution.

In view of the foregoing, it is recommended that the inert pigment in the prime coating be approximately thirty eight pounds. Therefore, it will be seen that in the prime coating there is a relatively higher proportion of titanium oxide.

Also, it is desirable in the finish coating to utilize a relatively high proportion of resins to pigment. Still further, it is desirable that the finish coating solution be somewhat thinner than the prime coating solution and therefore, the total solids contained in the coating solution or bath should be approximately 60% of the total weight of the coating solution or bath for the finish coating and approximately 70% for the prime coating, although the latter percentage may be increased to as high as 80%.

The aforesaid coating solutions or baths will provide an opaque white coating resembling enamel in appearance. By the simple expedient of adding suitable colored pigments or other coloring agents the coating may be given any desired color. Many suitable coloring agents will occur to a skilled chemist. For instance, iron black will produce a black coating, chrome yellow a yellow coating, and various iron oxide pigments will produce red or brownish coatings.

A coating solution or bath made up in accordance with the foregoing directions and formulas will possess approximately the correct viscosity for applying the coating by a dipping operation.

However, it is to be understood that this viscosity should be carefully regulated in order that the object may be dipped or immersed in the coating solution or bath with satisfactory results. Accordingly, a coating solution made up in accordance with these directions and formulas may be altered somewhat as to viscosity by the simple means of adding or taking away solvents, as the case may require. I have found that several factors should be considered in regulating the viscosity of the solution or coating bath. Among these are the temperature of the air, temperature of the coating solution, the absence or presence of draughts in the room, the shape of the object, the temperature of the object, and the way the object is hung or handled during the subsequent air drying and baking operations described hereinafter. Under normal conditions, that is where the temperature of the coating solution is approximately room temperature, where the room is reasonably free from draughts, where the object is treated at room temperature, and where the shape of the object is not unusual, I have found that the viscosity of the coating solution or bath for a dipping operation should be approximately twenty to thirty seconds, when measured on a viscosimeter utilizing a number four tip on a Ford cup.

If the coating solution or bath is to be applied to the object by a spraying operation, it is recommended that the viscosity of the solution be increased, that is, that the solution be heavier. The factors mentioned above for determining the viscosity for dipping also should be considered for a spraying operation. Additional factors in considering the viscosity for spraying application include the air pressure and assuming that a spraying booth is utilized, the rate of exhaust from the spraying booth. Since these factors vary considerably with each spraying operation, it is not possible to provide herein exact viscosities for each and every spraying operation. However, one skilled in the art can easily determine the desired viscosity suitable for his particular conditions. As a rule, however, more high boiling solvents or a relatively larger concentration of high boiling solvents should be employed if a spraying operation is employed than where a dipping method of application is employed.

As indicated above, the coating solution or bath is applied to the object by immersion, dipping, spraying or other suitable means. The amount of coating thus applied should be sufficient to provide a film weight of the coating solution in an amount of approximately two to three milligrams per square centimeter. This is regarded as a minimum in order that the present coating may operate effectively. Thinner coatings appear to suffice to provide a corrosion and rust resistant coating, but such thinner coatings usually do not have sufficient hiding power to provide a pleasingly appearing and wholly satisfactory coating. Also, such thin coatings tend to be removed too easily by mechanical abrasion. It is, therefore, desirable to utilize more than this minimum. It is recommended that from five to nine milligrams per square centimeter be employed. In fact, we have utilized as much as twelve to fifteen milligrams per square centimeter although these heavy coatings do not appear to add to the protective properties of the coating. However, such heavy coatings could, of course, be employed. After the object has been air dried, it is baked. This baking operation is accom-

plished by subjecting the object to increased temperatures. Approximately fifteen minutes at temperatures of from 360 to 375° F. have been found to suffice as have approximately 11 minutes at about 400° F.

Any suitable apparatus for air drying and baking the coating may be utilized although it is preferable that the air drying operation immediately precede the baking operation, and that the temperatures during the air drying operation be gradually increased during that operation until they approach the minimum temperature of the baking operation. In this connection one suitable form of apparatus for effecting the air drying and baking operation of the present coating is disclosed and claimed in our U. S. Letters Patent No. 2,375,173.

It will be understood, however, that but one coating may be utilized if desired and that more than two coatings also may be utilized, although we have found that a prime and a finish coating appears to produce satisfactory results.

An ice tray coated in accordance with the present invention possesses on its surfaces a sub-coating consisting of reaction products of the ferrous metal and the phosphates or chromates utilized in applying the sub-coating. Over this sub-coating the article possesses a prime and finish coating consisting of reaction or polymerization products of the alkyd resins, urea formaldehyde resins and melamine formaldehyde resins utilized as ingredients in the coating solution or bath. In addition, these prime finish coatings contain pigments, particularly titanium dioxide. It is our belief that these pigments are not simply present in the finish coating as unreacted particles within the polymerized or reaction products of the resins. Apparently said pigments enter the reaction itself which produces the polymerized and reaction product coating. At least they appear to provide focal points about which the polymerizing or reacting of the resins takes place. However, these observations merely represent our opinion in this respect.

Whatever the chemical explanation, the present novel coating provides an exceptionally effective corrosion and rust resistant coating which is particularly satisfactory for ferrous metal objects which are subjected to rigorous conditions. In particular, this coating is sufficiently flexible that it does not chip or is not otherwise removed from the article, even if the article is flexed or bent. Thus, the article may be relatively roughly handled without deleterious effects. An ice tray bearing the present coating may be removed from and placed in the refrigerator and may be roughly handled to remove the ice cubes without deleteriously affecting the coating. Furthermore, the present coating is sufficiently resistant to abrasion so that it is not easily scraped from the coated object. Therefore, an ice tray bearing the present coating may have a grid placed in it and may have said grid removed by prying, when necessary, to remove the ice cubes without breaking down the coating. Still further, ice or frozen materials do not adhere firmly to the present coating thus facilitating the removal of such materials.

The present coating is pleasing in appearance, does not react with rubber or the like so that rubber grids or inserts may be employed without producing black marks or other unsightly or deleterious effects, and may be safely used with edible products without in any way tainting them or affecting their taste. Therefore, ice trays or similar objects bearing the present coating may be

formed of ferrous metals, such as steel, and yet satisfactorily employed for the purposes for which they were intended.

We claim:

1. A ferrous metal ice tray for receiving materials to be frozen, said tray possessing on its material contacting surfaces an adherent protective coating comprising an iron phosphate and there-over a moisture repellent baked enamel-like flexible, adherent and abrasion resistant layer containing titanium dioxide and the combined polymerization products of an alkyd resin, a urea formaldehyde resin and a melamine formaldehyde resin.
2. A ferrous metal ice tray for receiving materials to be frozen, said tray possessing on its material contacting surfaces an adherent protective coating comprising an iron phosphate and there-over a baked enamel-like layer containing pigments including titanium dioxide and polymerization products of approximately 60 to 120 parts by weight of alkyd resins, approximately 12 parts to 100 parts by weight of urea formaldehyde resins and approximately 20 to approximately 120 parts by weight of melamine formaldehyde resins.
3. A ferrous metal ice tray for receiving materials to be frozen, said tray possessing on its material contacting surfaces, an adherent protective coating comprising an iron phosphate and there-over a flexible, adherent, moisture repellent and abrasion resistant baked enamel-like layer containing pigments including titanium dioxide and polymerization products of approximately 160 parts by weight of a drying oil modified glycerol phthalate resin, approximately 108 parts by weight of a non-drying oil modified glycerol phthalate resin, approximately 13 parts by weight of a urea formaldehyde resin and approximately 48 parts by weight of a melamine formaldehyde resin.
4. A ferrous metal ice tray for receiving materials to be frozen, said tray possessing on its material contacting surfaces an adherent protective coating comprising an iron phosphate and there-over a flexible, adherent, moisture repellent and abrasion resistant baked enamel-like layer containing pigments including titanium dioxide and polymerization products of approximately 160 parts by weight of a drying oil modified glycerol phthalate resin, approximately 108 parts by weight of a non-drying oil modified glycerol phthalate resin, approximately 13 parts by weight of a urea formaldehyde resin and approximately 48 parts by weight of a melamine formaldehyde resin.

ALBERT L. BUNTING.
ARTHUR C. SCHULTZ.