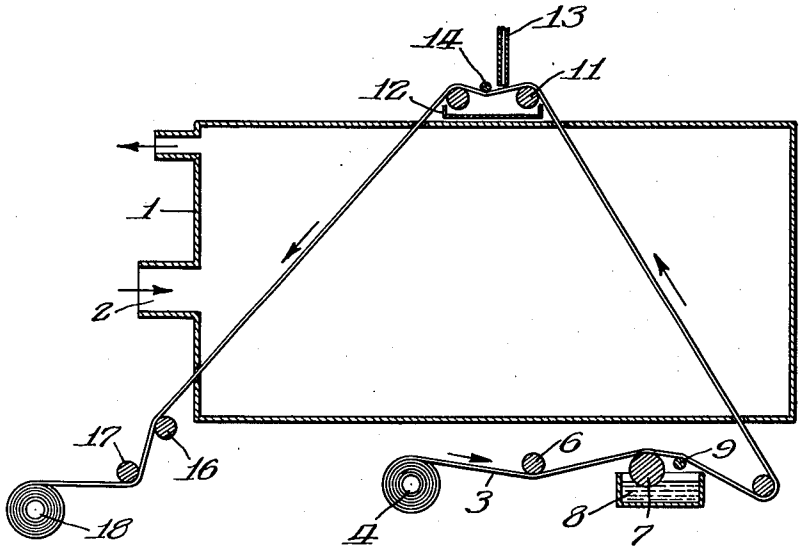
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TRANSPARENT HEAT-SEALABLE SHEETS CARRYING VAPOR PHASE CORROSION INHIBITORS

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TRANSPARENT HEAT-SEALABLE SHEETS CARRYING VAPOR PHASE CORROSION INHIBITORS

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This invention relates to vapor phase corrosion inhibition of metals, particularly iron, steel and other ferrous metals, and articles made therefrom, and is especially concerned with the production of new and highly useful transparent heat-sealable sheets carrying or embodying therein vapor phase corrosion inhibitors the vapors of which are gradually released, in use, to effect the inhibition of the corrosion of the metals or metal articles which are wrapped or otherwise enclosed in said sheets.

In U.S. Patent No. 2,829,080, transparent heat-sealable sheets are disclosed comprising a transparent organic film base essentially resistant to the passage therethrough of corrosion inhibiting vapors, a transparent organic covering film bonded to the film base and pervious to the passage therethrough of the corrosion inhibiting vapors, and a vapor phase corrosion inhibitor compatible with and embodied in said cover film.

The transparent heat-sealable vapor phase corrosion-inhibitor carrying sheets of the aforesaid U.S. patent constitute a marked improvement over sheet materials for such purposes previously known in the art, as is fully brought out in the said patent. It has, nevertheless, been found, in accordance with the present invention, that significant improvements result if, in place of the vapor phase corrosion inhibitors disclosed in said patent, certain particular materials, described below in detail, are utilized. Furthermore, it has been found, pursuant to the present invention, and as will also be set forth below, that additional improvements result by reason of the employment of particular organic film base and cover film materials, and in particular details of the arrangement of said materials.

In accordance with the present invention, as in the aforesaid patent, the transparent heat-sealable sheets comprise a transparent organic film base, which may or may not be a polymer but which is essentially resistant to the passage therethrough of corrosion inhibiting vapors, a transparent organic covering film which is bonded to said transparent organic film base and which is pervious to the passage therethrough of said corrosion inhibitor vapors, and a vapor phase corrosion inhibitor compatible with and embodied in or adjacent to said organic covering film or, in other words, in operative relation to said films.

Despite their excellent functioning in general, various of the vapor phase corrosion inhibitors disclosed in said patent, for example, the organic nitrites and inorganic nitrites, when embodied in the transparent films, cause a slight discoloration or yellowing of said sheets upon the passage of time, for instance, a few weeks, and which, under certain circumstances, may be regarded as somewhat objectionable even though the corrosion inhibiting properties of said sheets are in no way impaired. We have discovered, however, and among other things, that if the vapor phase corrosion inhibitor utilized is a straight chain C_6 to C_{10} alkanoic acid, or a C_7 to C_{11} aromatic monocarboxylic acid, or mixtures of one or more of said alkanoic and said aromatic monocarboxylic acids, the clarity of the sheets is not impaired and discoloration does not take place even after very prolonged periods of time. The C_6 to C_{10} alkanoic acids comprise caproic, enanthic, caprylic, pelargonic and capric acids. Typical

of the aromatic monocarboxylic acids are benzoic, toluic and tertiary butyl benzoic acid. These acids should, of course, be used in such proportions in or adjacent to the cover film as not unduly to impair the desired transparency or clarity of the finished sheet. Generally speaking not more than about 5% by weight of any one of said acids can be incorporated into the cover film without causing or tending to cause a slight haze. We have found, however, that mixtures of said acids in many cases can be used in substantially greater proportions without causing haze. Thus, for instance, using equal weights of benzoic acid and pelargonic acid as the vapor phase corrosion inhibitor, as much as about 20% by weight can be incorporated into the cover film without impairing the clarity of said film or of the finished sheet. In general, where mixtures of benzoic acid with one or more of the aforesaid alkanoic acids notably pelargonic acid, are utilized, a good working range is from 1 to 3 parts of benzoic acid with from 3 to 1 parts of pelargonic acid or others of said alkanoic acids or mixtures of said alkanoic acids, said parts being by weight, and particularly preferred are approximately equal parts by weight of the benzoic and alkanoic acid or acids.

The transparent organic film bases and transparent covering films may be selected from those which have been disclosed in the aforesaid patent and the techniques of producing the final transparent heat-sealable sheets containing the vapor phase corrosion inhibitors disclosed above in this specification may be those which are described in said patent, the pertinent portions of said patent being incorporated herein by reference.

We have found, however, that exceptionally satisfactory results are obtained by using an ethylene glycol terephthalic acid polymer ("Mylar") as the base film in conjunction with a top coating or covering film of transparent cellulose acetate butyrate and an intermediate layer of a transparent adhesive, notably, an acrylonitrile butadiene copolymer. The base film in this particular embodiment is desirably 0.5 to 1.5 mil thickness; the top coating or film is advantageously about 0.3 to 0.4 mil thickness; and the intermediate layer, which is of adhesive character, is about 0.6 to 0.7 mil thickness. While all of the aforesaid volatile corrosion inhibitor could be incorporated into the covering film, it has been found to be especially advantageous to include a portion, and especially the major portion, of said corrosion inhibitor in the intermediate layer of transparent adhesive where this technique of making the finished sheets is utilized. This results in effectively meeting the problem of blocking or cracking. Thus for example, where a polyacrylate transparent resin is used as the top or covering film, it not infrequently tends to crack when the finished sheet is bent. If a softer covering film is used as, for instance, by adding plasticizers, the cracking problem is eliminated but then blocking is encountered when the finished film is made into a bag. The inclusion of the alkanoic acids or the aromatic monocarboxylic acids, or mixtures of said acids, aids markedly in overcoming blocking when added to the intermediate adhesive layer, notably acrylonitrile-butadiene copolymers, and the combination therewith of a top covering film of transparent cellulose acetate butyrate most effectively serves to overcome the foregoing practical problems.

In addition to the transparent base films disclosed in the foregoing patent of which ethylene glycol-terephthalic acid polymers, commonly designated as ethylene terephthalate films, are especially useful in the practice of the present invention, other transparent materials which are particularly satisfactory for use as base films are the polycarbonates such as those sold under the designation "Lexan" (General Electric Company), and the polyester

product sold under the designation "Videne" (Goodyear Tire & Rubber Company). All of these may be classed as polyesters, the polycarbonates constituting a special class of polyesters. Suitable polycarbonate films are, in general, esters of aromatic glycols or bisphenols with carbonic acid, illustrative of which are reaction products of bisphenol A and phosgene, or reaction products of bisphenol A and dimethyl carbonate. Other suitable polyester films comprise, generally, esters of dibasic aromatic acids with glycols. The polycarbonates and the polyesters and methods for their production are, per se, known in the art. The films utilized in accordance with our present invention should most desirably be flexible.

It is especially advantageous to utilize a transparent adhesive intermediate the transparent base film and the transparent covering film. Such transparent adhesives are most desirably rubbery materials. Particularly satisfactory results have been obtained with copolymers of acrylonitrile and butadiene, a typical example of which is the product sold under the designation "Chemigum" N–6B (Goodyear Tire & Rubber Company) which contains approximately 32% by weight of acrylonitrile. Other typical suitable transparent adhesives are rubbery acrylonitrile-butadiene copolymers sold under such designations as "Hycar" 1512, "Hycar" 1552, "Hycar" 1561, "Hycar" 1577 (B. F. Goodrich Chemical Co.); "Chemigum" 235, "Chemigum" 245 (Goodyear Tire & Rubber Company); "Butaprene" NSP 169 (Firestone Tire and Rubber Company), and the like. These substances are per se known in the art. It is preferred to utilize such commercial products as contain antioxidants but, if desired, any suitable antioxidant can be incorporated therein.

The thickness of the transparent heat-sealable sheets of the present invention is, of course, variable. In all instances, however, they should not be so thick as to interfere with their flexibility and the ability to utilize the same for wrapping and packaging purposes. In general, the finished transparent sheet desirably has a thickness of about 0.5 to about 5 to 10 mils, particularly, from about 1 to 5 mils. The transparent organic film base, for example, may have a thickness of the order of 0.5 to 1.5 mil and the thickness of the transparent organic covering film may, for instance, also be of the order of 0.3 to 0.5 mil but may be of a thickness of 1 to 3 or 5 mils so that the total thickness may be, for instance, from 1 to 5 mils for the final finished transparent sheet.

The amount of the vapor phase corrosion inhibitor which is embodied in the transparent organic covering film or, in other words, directly into or adjacent said latter film or in operative relation to said film, is somewhat variable, depending, among other things, upon the desired useful life of the sheet from the standpoint of its effectiveness to inhibit the corrosion of metals wrapped therein. Generally speaking, the vapor phase corrosion inhibitor is utilized in an amount sufficient to constitute, by weight, from about 0.1 to about 1 or 2 grams per square foot of the area of the transparent sheet. Preferably, the amount of vapor phase corrosion inhibitor used will, in most cases, range from about 0.2 to about 0.6 gram per square foot of area of the sheet. In terms of the amount, by weight, of the vapor phase corrosion inhibitor based on the weight of the transparent organic cover film, good results are obtained, in at least most cases, with the vapor phase inhibitor comprising from about 5 to about 20%, by weight, of the cover film.

The following table illustrates specific examples of transparent heat-sealable sheets made in accordance with the present invention. It will be understood that these examples are given merely by way of illustration and are not intended in any way to be limitative of the full scope of the invention.

Table

Example No.	Base Film (Impermeable to Vapors)	Cover Film	Intermediate Adhesive Layer	Vapor Phase Corrosion Inhibitor and Percentage by Weight Thereof Based on Cover Film
1	Ethylene glycol-terephthalic acid polymer ("Mylar").	Cellulose Acetate Butyrate		Pelargonic acid (5%).
2	do	do	Chemigum N-6B.	Equal parts of pelargonic acid and benzoic acid (15%) equally distributed in adhesive layer and in cover film.
3	do	do	do	Equal parts of pelargonic acid and benzoic acid (15.4%) 75% of which is distributed in adhesive layer and 25% in cover film.
4	do	Vinyl chloride-vinyl acetate copolymer ("Vinylite VYNS").		Equal parts of pelargonic acid and benzoic acid (12%).
5	do	Polyethyl acrylate ("Rhoplex WN-80").		1 part pelargonic acid and 2 parts benzoic acid (10%).

NOTE.—Deposit of the cover film in each of the above examples is from organic solvent solutions, specifically, acetone solutions of the cellulose acetate butyrate, and of the "Chemigum" where used, on the base film.

The aforesaid coatings, as indicated above, can be applied to the base film, for instance, the ethylene glycol-terephthalic acid polymer film, in any suitable manner and through various existing types of coating equipment. The accompanying drawing shows, in schematic form, an arrangement of equipment which has been found to be very satisfactory, particularly from the standpoint of economy in that the intermediate adhesive and the top or cover film are applied on one side of the base film in a single pass of the said base film.

In the accompanying drawing, numeral 1 indicates a drying oven through which air, preferably previously heated air, from conduit 2 is passed, advantageously sufficiently rapidly so as to avoid the formation of air-organic solvent concentrations within the explosive range where certain organic solvents are involved. It is preferred that the drying oven house a bank or banks of infra red heaters in order to reduce or eliminate the tendency of surface crusting and entrapment of organic solvent. A film or sheet 3, most desirably continuous, of the ethylene glycol-terephthalic acid polymer is fed from a roll 4 thereof beneath a tensioning roller 6 over a coating roller 7 disposed over a trough 8 carrying an organic solvent solution of the transparent adhesive material and, desirably, at least a part of the alkanoic acid and/or aromatic monocarboxylic acid. The underside of the film or sheet 3 picks up an excess coating from the roller 6 of the said solution. The thus excess coated film or sheet passes into contact with a wire bar 9, namely, a metal bar wrapped with wire. The said organic solvent solution passes through the crevices in the wire bar and then flows to form a smooth coating on the sheet or film, excess organic solvent solution draining back into the trough 8. The coated film or sheet then passes into the drying oven which, in the illustrative example of organic solvent solution of the adhesive material, may be maintained at about 200 degrees F. The organic solvent is essentially evaporated and the film or sheet then passes to a de-

vice for applying the top or cover film, for instance, cellulose acetate butyrate. Since the dried first coating applied to the ethylene glycol-terephthalic acid film or sheet may be somewhat tacky, the top or cover coating or film should be applied before the finished film or sheet is wound into a roll. After the tacky rubbery coating solution is applied and dried, the said base coated film is passed out of the drying oven and over a roller **11** disposed over a trough **12**. It will be noted that the adhesive layer is now uppermost. An organic solvent solution of the cover coating material containing the added alkanoic acid and/or aromatic monocarboxylic acid is then discharged through a sluice **13** into the dried tacky surface and the quantity and even distribution thereof is controlled by a wire bar **14**, excess solution dropping into the trough **12**. The film or sheet then passes back into drying oven **1** to effect removal of the organic solvent and then passes out of said oven and is cooled by air over a chill roll **16**, then over rollers **17** and finally to windup roller **18** where the finished film or sheet is wound into rolls. The equipment should be operated to avoid condensation of atmospheric moisture on the applied coatings before the film or sheet enters the drying oven so as to avoid haziness in the finished films or sheets. This can readily be accomplished by controlling the rate of movement of the film or sheet, the relative humidity, temperature and solvent volatility through the selection of proper solvents.

In an illustrative example, a 15% solution of "Chemigum" N–6B in acetone is very suitable as the solution from which the adhesive layer is laid down. The "Chemigum" N–6B is first advantageously worked on a rubber mill for a few minutes and then cut into small pieces to facilitate its solution in the acetone. For the cover coating, a typical illustrative coating solution is a 30% solution in acetone of a transparent cellulose acetate butyrate.

What is claimed as new and desired to be protected by Letters Patent of the United States is:

1. A transparent heat-sealable sheet comprising a transparent organic film base essentially resistant to the passage therethrough of corrosion inhibiting vapors, a transparent organic covering film bonded to said film base and pervious to the passage therethrough of said corrosion inhibiting vapors, and, as a vapor phase corrosion inhibitor compatible with and in operative relation to said cover film, at least one member of the class of C_6 to C_{10} alkanoic acids.

2. A sheet in accordance with claim 1, wherein said transparent organic film base is an ethylene glycol-terephthalic acid polymer, and the covering film is cellulose acetate butyrate.

3. A transparent heat-sealable sheet comprising a transparent organic film base essentially resistant to the passage therethrough of corrosion inhibiting vapors, a transparent organic covering film bonded to said film base and pervious to the passage therethrough of said corrosion inhibiting vapors, said sheet having a thickness of about 0.5 to 5 mils, and, as a vapor phase corrosion inhibitor compatible with and in operative relation to said cover film, up to 20%, by weight of said covering film, of at least one member of the class of C_6 to C_{10} alkanoic acids.

4. A transparent heat-sealable sheet comprising a transparent organic film base essentially resistant to the passage therethrough of corrosion inhibiting vapors, a transparent organic covering film bonded to said film base and pervious to the passage therethrough of said corrosion inhibiting vapors, said sheet having a thickness of about 0.5 to 5 mils, and, as a vapor phase corrosion inhibitor embodied in said covering film in a total amount of from about 5 to 20% by weight of said covering film, a mixture of benzoic acid and at least one member selected from the group consisting of C_6 to C_{10} alkanoic acids.

5. A sheet in accordance with claim 4, wherein said transparent organic film base is an ethylene glycol-terephthalic acid polymer, and the covering film is cellulose acetate butyrate.

6. A transparent heat-sealable sheet comprising a transparent organic film base resistant to the passage therethrough of corrosion inhibiting vapors, a transparent organic covering film bonded to said film base and pervious to the passage therethrough of said corrosion inhibiting vapors, said sheet having a thickness of about 0.5 to 5 mils, and, as a vapor phase corrosion inhibitor in operative relation to said covering film in a total amount of from about 5 to 20% by weight of said covering film, a mixture of approximately equal parts of benzoic acid and pelargonic acid.

7. A transparent heat-sealable sheet comprising a transparent ethylene glycol-terephthalic acid polymer film base essentially resistant to the passage therethrough of corrosion inhibiting vapors, a transparent organic covering film bonded to said film base through a layer of a transparent adhesive and pervious to the passage therethrough of said corrosion inhibiting vapors, and a vapor phase corrosion inhibitor in operative relation to said covering film and being present in a total amount of from about 5 to 20% by weight of said covering film, said vapor phase corrosion inhibitor being selected from the class consisting of at least one member of the C_6 to C_{10} alkanoic acids.

8. A transparent heat-sealable sheet comprising a transparent ethylene glycol-terephthalic acid polymer film base essentially resistant to the passage therethrough of corrosion inhibiting vapors, a transparent covering film bonded to said film base through a transparent adhesive and pervious to the passage therethrough of said corrosion inhibiting vapors, and, as a vapor phase corrosion inhibitor embodied in said covering film in a total amount of from about 5 to 20% by weight of said covering film, a mixture of approximately from 1 to 3 parts of benzoic acid with from 3 to 1 parts of pelargonic acid.

9. A transparent heat-sealable sheet comprising a transparent polyester film base essentially resistant to the passage therethrough of corrosion inhibiting vapors, a transparent coating on said film base which coacting comprises an acrylonitrile-butadiene copolymer, and a transparent cellulose acetate butyrate covering film embodying therein at least one member selected from the class consisting of C_6 to C_{10} alkanoic acids.

10. A transparent heat-sealable sheet comprising a transparent ethylene glycol-terephthalic acid polymer film base, a transparent coating on said film base which coating comprises an acrylonitrile-butadiene copolymer, and a transparent cellulose acetate butyrate covering film embodying therein a small percentage by weight of each of benzoic acid and pelargonic acid.

11. A transparent heat-sealable sheet comprising a transparent ethylene glycol-terephthalic acid polymer film base, a transparent coating on said film base which coating comprises an acrylonitrile-butadiene copolymer embodying from about 5 to 6% by weight of each of benzoic acid and pelargonic acid, and a transparent cellulose acetate butyrate covering film embodying therein a small percentage by weight of each of benzoic acid and pelargonic acid.

12. A transparent heat-sealable sheet comprising a transparent ethylene glycol-terephthalic acid polymer film base, a transparent coating on said film base which coating comprises an acrylonitrile-butadiene copolymer embodying from about 5 to 6% by weight of each of benzoic acid and at least one member of the group of C_6 to C_{10} alkanoic acids, and a transparent cellulose acetate butyrate covering film embodying therein from 1 to 3% by weight of each of benzoic acid and at least one member of the group of C_6 to C_{10} alkanoic acids.

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