ACRYLONITRILE-ETHYL ACRYLATE (WT. RATIO 25:75 TO 40:60) COPOlysYMER COATING

PAPER INPREGNATED WITH NON-VOLATILE HYDROCARBON (LIQ. PT. BELOW 200 °F)
The present invention relates to coated, impregnated paper. More particularly, the invention relates to paper impregnated with a hydrocarbon liquid or wax and carrying on one side only a grease-resistant polymer coating.

It is known that paper coated with a polymer of high molecular weight consisting essentially of a minor amount of acrylonitrile copolymerized with a major amount of ethyl acrylate (or coated with a polymer formed from similar copolymerizable monomers) possesses good resistance to penetration by grease when the grease is applied to the side of the paper carrying the coating. It is further known that paper which has been impregnated with a non-volatile solid or liquid hydrocarbon possesses good resistance to penetration by water vapor.

The discovery has now been made that wax or hydrocarbon oil impregnated paper carrying a copolymer coating of the type described can be made by a two-step process involving complete immersion of the paper in the hydrocarbon in liquid form. In the first step, one side of the paper is coated with the polymer. In the second step, the paper is passed directly into and through a bath of the hydrocarbon in liquid form whereby the entire body of the paper becomes impregnated with the hydrocarbon which acts as agent rendering the paper resistant to penetration by water vapor. The invention depends primarily on the discovery that the polymer and the wax are so mutually repellent that even at bath temperatures up to 200° C. the polymer is substantially unaffected by the wax, and substantially none of the wax adheres thereto as the sheet is removed from the bath.

The product of the invention is thus paper uniformly impregnated with a non-volatile hydrocarbon liquid or liquid and carrying externally on one side only a hard, glossy and grease-resistant polymer coating.

The invention does not depend upon the particular way in which the first step is performed. Thus the polymer may be applied in a solvent solution form or as a hot melt. In practice, application of the copolymer in aqueous emulsion form is preferred, the aqueous content of the emulsion being removed by drying before the paper is passed through the impregnating bath. Enough of the polymer is applied to render the paper grease-resistant, and the necessary amount may be applied as one coating or as a plurality of coatings with intermediate dryings. The product of this step is paper raw stock carrying on one side a hard, flexible, hydrophobic, glossy polymer coating.

In the second step, the paper is immersed in the hydrocarbon bath until at least sufficient has been absorbed so that the paper when removed from the bath has a low water vapor transmission value. The temperature of the bath should be sufficiently high so that the hydrocarbon is entirely a liquid of water viscosity permitting uniform impregnation with rapid elimination of the air content of the paper. The polymer coating is not rendered tacky by the process even at bath temperatures as high as 200° F. and thus the paper may be carried down into, through, and out of the bath with the coated side of the paper in direct contact with a steel roll or bar.

As the paper leaves the bath, the hydrocarbon liquid flows readily as water flows from a surface treated with paraffin wax. Surface (unadsorbed) hydrocarbon liquid may be removed from the web side by squeegee rolls, air jets or other convenient means, after which the paper is cooled and rolled.

Paper produced by the foregoing process is illustrated in the attached drawing, which is a schematic cross-section of a sheet produced thereby. In the drawing 1 represents paper impregnated with a non-volatile hydrocarbon having a liquefaction point below 200° F., and 2 represents the ethyl acrylate-acrylonitrile copolymer coating thereover.

The polymer referred to consists essentially of copolymerized acrylonitrile and ethyl acrylate in weight ratio between about 25:75 and 40:60. The copolymer is thus essentially a linear carbon chain or paraffin polymer having nitrite and carbethoxy groups attached thereto. Additional substituent groups may be present for diluent or other purposes such as alkyl, acid, aroyl, acetoxy, ketone or chloro groups. The polymers are prepared by copolymerization of appropriate monomer mixtures, and these additional groups may be introduced by addition of monomers carrying the desired groups. Suitable monomers include methacrylonitrile, ethyl methacrylate, vinyl isocyanate, vinyl acetate, maleic anhydride, maleic acid, acrylic acid, vinyl alcohol, styrene, p-methyl styrene, p-chloro-methyl styrene, acrylonitrile , ethyl acrylate, vinyl acetate, vinyl methyl ketone, and vinyl chloride.

The number of such substituent groups in the polymer is minor (less than 10% of the number of the nitrile groups plus the carbethoxy groups) and thus the groups do not affect the characteristic properties of the polymers.

Hydrophilic radicals, particularly carboxy groups are advantageous as these groups increase the contact angle between the hydrocarbon liquid and the polymer on the paper causing the hydrocarbon impregnating agent to flow off more rapidly than would otherwise be the case.

The molecular weight of the polymer should be at least about 50,000 to form a film of good flexibility, durability and non-blocking properties.

The polymer may contain dyes, one or more oil soluble dyes such as Nigrosine Base CF or Acetin Blue and pigments such as phthalocyanine blue and organophilic grade titanium dioxide white so as to provide a colored coating on the paper.

When the polymer is applied in emulsion form, the aqueous phase may contain a small amount of trimethylolmelamine or other water-soluble thermosetting melamine-formaldehyde or urea-formaldehyde condensate. When the paper is heated the condensate polymerizes tending to improve the hardness and grease resistance of the coating as a whole.

The hydrocarbon liquid used in the impregnation step may be any of the materials hereinafter employed for the purpose. Thus the hydrocarbon may be solid pastes or normally liquid, such as petroleum or the petrolatum oil customarily used in the manufacture of loin paper. On the other hand, the hydrocarbon may be a normally solid moderately low melting material such as the paraffin wax customarily used for the manufacture of the semi-transparent waxed paper of commerce. Higher melting paraffin or microcrystalline waxes may be used such as commonly used in manufacture of bread wrap. In general, best resistance to transmission of water vapor occurs when the hydrocarbon used is a wax, and sufficient is left on the sheet to form a continuous coating.

The wax may contain pigments, dyes, perfumes and other materials as have heretofore been employed in the manufacture of waxed paper.

The paper of the present invention finds principal use for the packaging where moisture vapor resistance and grease resistance are both required. It is suitable for
the packaging of meat, fish and materials having a delicate flavor which must be protected, such as cottage cheese and baked goods.

The invention will be more particularly described with reference to the examples. The examples represent specific embodiments and are not to be construed as limitations thereon.

**Example 1**

The following illustrates one method of preparing coated, impregnated paper according to the present invention.

Sheets of coating raw stock of 51 lb. basis weight (25" x 38"/500 ream) were coated with an aqueous acrylonitrile-ethylene acrylate emulsion applied at 44% solids by means of a 0.005" Bird applicator. Three coats of emulsion were applied, and the sheets were oven-dried at 220° F. for three minutes after each coat; the total weight of the polymer on the paper was 13 lb. (25" x 38"/500 ream). The sheets carried a clear, hard, glossy polymer coating on one side, and were raw paper on the other.

The sheets were cut to 5" x 7". Samples were retained as controls and the remainder passed through a bath of paraffin wax (M.P. 133-135° F.); the bath contained a horizontal ½" stainless steel pipe and the sheets were passed under the pipe to effect complete impregnation, the coated (polymer) side of each sheet being the "up" side. The sheets showed no tendency to adhere to the pipe.

As the sheets were pulled from the bath, the wax completely ran off the polymer coated side without wetting. Excess wax was doctoried off the opposite side by means of a smooth metal rod. The treatment did not significantly alter the color, hardness or the gloss of the polymer coatings.

Additional controls were prepared by passing sheets of the raw stock through the paraffin bath without polymer coating.

The grease resistance values of the samples were determined by TAPPI method T454-M44 (using turpentine) and the water vapor permeability by the weight increase of calcium chloride in a cup having a top capped with the paper under test. Results are as follows:

<table>
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<tr>
<th>Sample</th>
<th>Grease Resist. (mil.)</th>
<th>Water Vapor Permeability, gm./100 in.2/4 hr.</th>
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<tr>
<td>1</td>
<td>Polymer only (control)</td>
<td>&gt;800 1 20.9  1.6</td>
</tr>
<tr>
<td>2</td>
<td>Polyacrylamide bath only (control)</td>
<td>N.D. 0 24.8  1.6</td>
</tr>
<tr>
<td>3</td>
<td>Polymer first, then paraffin</td>
<td>&lt;800 1 20.9  1.6</td>
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</table>

1Turpentine evaporated before penetrating film.
2At 75° F. and 65% R.H.
3At 100° F. and 60% R.H.

The polymer emulsion was prepared by copolymerizing at pH 9 for 6 hours acrylonitrile with ethyl acrylate in 30:70 weight ratio using ammonium persulfate as the catalyst and Du Pontol C (an anionic high alkyl sulfate) as emulsifier; the emulsion solids was 45%, the remainder being water. The residual monomers were removed by further redox treatment. No emulsion particles were larger than 6μ. The molecular weight of the polymer by the Steainger method based on intrinsic viscosity was about 100,000.

**Example 2**

The process of Example 1 was repeated except that the wax bath was replaced by a clear white mineral oil (Nujol) bath at room temperature, and after impregnation the excess oil was evaporated off. The mineral oil showed no tendency to wet the polymer coating and ran off in the same manner as molten paraffin wax. A sheet was obtained resembling the test sheet material of Example 1, except that the flexibility was greater.

**Example 3**

The procedure of Example 1 was repeated except that the polymer was applied in the form of a 10% by weight solution in anhydrous methyl ethyl ketone. The solution was viscous and was applied to a thickness of about 0.0015" by Bird applicator (three 0.005" coatings with intermediate oven dryings) at 220° F. for 5 minutes to remove solvent. After wax impregnation the sheets closely resembled the sheets of Example 1.

I claim:

1. Paper uniformly impregnated with a non-volatile hydrocarbon having a liquefaction point below 200° F. and carrying externally on one side only a hard and glossy grease-resistant coating of a polymer having a molecular weight in excess of about 50,000 consisting essentially of copolymerized acrylonitrile and ethyl acrylate in weight ratio between about 25:75 and 40:60, said paper being resistant to passage of water vapor there through.

2. Paper according to claim 1 wherein the hydrocarbon is paraffin wax.

3. Process which comprises first coating one side of paper raw stock with a polymer having a molecular weight in excess of 50,000 consisting essentially of copolymerized acrylonitrile and ethyl acrylate in weight ratio between about 25:75 and 40:60, and then passing the stock carrying said coating through a body of non-volatile liquid hydrocarbon having a liquefaction point below 200° F. thereby impregnating said stock with said hydrocarbon without wetting the polymer coating thereon whereby a paper is formed which carries externally a hard and glossy grease-resistant coating on one side only, and which is resistant to passage of water vapor there through.

4. Process according to claim 3 wherein the polymer is applied to the paper as an aqueous emulsion and the paper is dried before it is impregnated with the hydrocarbon.

5. Process according to claim 3 wherein the hydrocarbon is paraffin wax having a melting point between 130° and 150° F.

6. Paper uniformly impregnated with a non-volatile hydrocarbon having a liquefaction point below 200° F. and carrying externally on one side only a hard glossy grease-resistant coating of a polymer having a molecular weight in excess of about 100,000 consisting essentially of copolymerized acrylonitrile, ethyl acrylate and acrylic acid in about 30:65:5 weight ratio.

References Cited in the file of this patent

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<table>
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<tr>
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