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PACKAGE COATED WITH PARAFFIN AND A POLYMERIZED PRODUCT OF A CYCLO- PENTADIENE

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This invention relates to an improved package. It more particularly relates to a package for liquid or solid consumer goods, and in particular foods, which is capable of being sterilized.

Solid and liquid foods are preferably packaged in a form in which they may be distributed and stored and sold to the individual consumer. The coating of the packages to render the same impermeable to micro-organisms such as germs followed by sterilization insures that the contents will remain in unobjectionable and stable condition. Packing methods of this type are absolutely essential in the sale and distribution of milk and other foods and goods which must be kept free from contamination for hygienic purposes. Up to the present, glass containers have received the most wide-spread use for this purpose since the same will stand up under any sterilization temperatures. Glass containers, however, have the disadvantage in that their relatively high cost often prohibit their use as a throw-away container and the empty containers must be returned and collected.

Paper and paper-board packages and containers have been used in the food and related industries. These containers have their inner and/or outer surfaces coated with paraffin or artificial resin varnishes. The cost of these air-tight packages is so relatively small that the empty packages may be thrown away or destroyed as a useless waste material.

Low-cost packages and containers produced from waxed paper and waxed paper-board materials are very advantageous in view of their extremely low cost and the easy manner in which they may be produced. These waxed paper and paper-board packages and containers, however, have the disadvantage that they will only withstand temperatures up to approximately 50° C. due to the low melting point of the paraffin grades conventionally used. At temperatures in excess of this, leakages and a detrimental influence on the taste of the content of the package must be expected. Thus, it is impossible to sterilize the filled, sealed package of this type. This entails the necessity of a prior sterilization of the material to be packed which has the disadvantage that mold or other harmful micro-organisms may be introduced into the material to be packed by both the empty package and the filling operation.

One object of this invention is a package which may be produced in a simple manner at low cost and which will not deteriorate at sterilization temperatures. This and still further objects will become apparent from the following description:

It has now been found that the disadvantages of the prior art are not encountered if the sizing, lining and/or coating of packages consisting of paper, paper-board or similar material is effected with paraffin grades having a melting point which ranges above about 90 to 120° C., i. e. hard waxes.

It has been found that paraffins of high melting point

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produced by the catalytic hydrogenation of carbon monoxide are particularly well suited for this purpose.

It has further been found, in accordance with the invention, that paraffins of a very high melting point and of a low melting point from the catalytic hydrogenation of carbon monoxide may be combined to form sizes and coatings for packages which will meet all the requirements as to use with respect to temperature resistance and hardness. It has been found that it is possible to increase the adhesiveness of the paraffin mixture to the walls of the package which may, for example, consist of metal, paper or textile by adding conventional materials such as esters, resins or gelatines.

It is possible to produce the containers in accordance with the invention in the identical manner that the containers with the paraffin grades of the low melting point previously used were produced. The impregnation and/or coating of the paper, paper-board, textile and similar materials with the hard waxes, in accordance with the invention, is effected in the identical manner as the coating was with the paraffin grades of the lower melting points previously used except that a corresponding increase in the operating temperature is necessary. In addition, the manufacture, the handling and sealing of the packages in accordance with the invention requires no change of equipment from the conventional equipment and procedures used at the present time.

The high softening temperatures of the hard waxes and their chemical resistance permit sterilization temperatures of as high as approximately 90° C. Milk and similar foods which are conventionally sterilized and pasteurized at about 75 to 80° C. may be freed from micro-organisms in the usual manner after being filled into the package which has been made liquid-tight with the hard paraffins.

The use of the hard wax, in accordance with the invention, is not limited to the coating and/or impregnation of packages of paper, paper-board and similar materials. It may be used in an analogous manner to coat the inner surfaces of metal containers such as of cans or tubes. Containers so coated may be sterilized with their contents at temperatures of as high as 90° C. without affecting the taste of the contents or injuring the inner coating layer.

It is of particular advantage, in accordance with the invention, to use hydrocarbons which are produced by polymerizing cyclopentadien or dicyclopentadien. The high melting hydrocarbons of this type may be produced from cyclopentadien or dicyclopentadien which are present, for example, in the first runnings of the distillation of raw benzene, by heating them to elevated temperatures with or without the use of catalysts. It has been found particularly advantageous to heat the starting material to about 150 to 250° C. without the use of catalysts. This results in the production of hydrocarbons which contain several five-membered rings and have a melting point which ranges above 100° C., and, in some cases, even in excess of 200° C. A still further improvement of these high-melting hydrocarbons is possible by fractional distillation in vacuo, by selective extraction and/or hydrogenation.

These high-melting point hydrocarbons obtained by the polymerization of cyclopentadien or dicyclopentadien should be mixed with the paraffin hydrocarbon of a high melting point, i. e., the hard waxes. 2-70% of this polymerization product may be mixed with 98-30% of the hard wax, such as slate paraffin, hard paraffin, or other waxes. It is preferable to use mixtures containing 5-20% of the polymerization product of the cyclopentadien or dicyclopentadien, and 80-95% of the high-melting paraffins.

The high-melting paraffins, i. e. the hard waxes, exhibit a certain brittleness at low temperatures, which, in certain cases, is undesirable for production of the containers in accordance with the invention. It has been found that this disadvantage may be overcome, if necessary or desired, by mixing the high-melting paraffins with softening materials prior to use. Examples of materials which are suitable for this purpose include high-boiling hydrocarbons which have been found in small quantities to impart a sufficient elasticity to the high-melting paraffins without detrimentally influencing the contents of the package due to their completely inert properties.

The lining and/or coating of metal containers may be effected by immersing, brushing, or spraying. Even very thin layers of, for example, 30–40 grams of paraffin per square meter provide a sufficient and durable protection of the surface of, for example, sheet iron against corrosion from the contents of the package.

The process, according to the invention, uses hydrocarbons for the temperature-resistant impregnation of containers produced from paper, paper-board, textiles, or for the coating of containers produced from metal and other materials. The melting point of the hydrocarbon mixtures used must be so high that it is possible to sterilize the filled package. For this reason the hydrocarbon mixture used must contain larger portions of high molecular weight aliphatic or cyclic hydrocarbons. Low molecular weight hydrocarbons should be present only to the extent that the melting point will not range below 90° C.

The adhesiveness of the mixtures of high melting point hydrocarbons used in accordance with the invention is largely dependent on the brittleness of the material. Soft hydrocarbons adhere better in and to the surfaces to be coated therewith. The adhesiveness of the hydrocarbon mixtures used in accordance with the invention may considerably be improved by softeners of the conventional type and, for example, by polyethylene.

Further details are to be seen from the following examples which are given for illustration and not limitation.

Example 1

By means of the catalytic carbon monoxide hydrogenation there was produced a hard paraffin which substantially contained only hydrocarbons boiling above 460° C. It had a solidification point of 98° C., a penetration number of 1.1 and an average molecular size of C_{48} . This hard paraffin was melted and a paper cup was immersed into the melt. The paraffin-coated paper cup was subsequently put into a drying chamber heated to 120° C. where it was left for several hours. During this time, part of the paraffin coating was sweated off. Approximately 15 grams of paraffin per square meter of paper remained back. A paper cup thus impregnated with paraffin resisted temperatures of as high as 100° C.

Example 2

A melt of hard paraffin produced by the Fischer-Tropsch synthesis and substantially containing only hydrocarbons boiling above 380° C. and having a solidification point of 95° C., a penetration number of 1.9 and an average molecular size of C_{41} was used for the impregnation of paper. The paper to be impregnated was immersed into the paraffin melt and subsequently sweated off at 120° C. for a longer period. From the paper thus treated there were produced paper bags which during the sterilization of milk previously filled in resisted temperatures of as high as 95° C.

Example 3

The hard paraffin used in Example 1 was extracted by means of a heptane fraction. This resulted in an extracted fraction which had a solidification point of 110° C. and a penetration number of 0.1. A paper cup was

immersed into the melt of this paraffin and subsequently placed for a longer period into a drying chamber heated to 130° C. A part of the paraffin was thereby removed by sweating off. The paper cup thus treated was completely temperature-resistant up to 110° C.

Example 4

80 parts by weight of a petroleum slab paraffin having a solidification point of 52° C. was mixed with 20 parts by weight of the hard paraffin used in Example 1. A container consisting of thin paper-board was immersed into the melted paraffin mixture. A part of the paraffin coating taken up was sweated off at 120° C. in a drying chamber. The quantity of paraffin remaining back on the paper-board was approximately 15 grams per square meter of paper-board. Thereafter, the container was completely temperature-resistant up to 60° C.

Example 5

70 parts by weight of the petroleum slab paraffin used in Example 4 were mixed with 30 parts by weight of the hard paraffin used in Example 1. A paper cup was immersed into the melted paraffin mixture and subsequently heated for a longer period at 120° C. in a drying chamber thereby sweating off part of the paraffin. Thereafter, the paper cup was completely temperature-resistant up to 70° C.

Example 6

A web of paper was passed through a heated mixture consisting of 40 parts by weight of the petroleum slab paraffin used in Example 4 and 60 parts by weight of the hard paraffin used in Example 1. Following this treatment, the paper was conducted for a longer period through a drying chamber heated to 120° C. The paper thus impregnated was used for the production of bags which were filled with milk. The filled containers could be heated to temperatures of as high as 80° C. without detrimentally affecting their contents.

Example 7

Dicyclopentadien was heated for about 10 hours at approximately 200° C. This resulted in the formation of polymerization products of dicyclopentadien which were hydrogenated at 140–150° C. and slightly elevated pressure with the use of nickel catalysts. The hydrogenated polymerization product was dissolved in hot benzene and separated from insoluble products by filtration. By cooling the filtrate, hydrogenated pentameric cyclopentadien was obtained in the form of a white powder the melting point of which was 290–310° C.

By mixing 90 parts by weight of the hard paraffin used in Example 1 and 10 parts by weight of the hydrogenated pentameric cyclopentadien, a hydrocarbon mixture was obtained the pour point of which was 185° C. This wax was melted and a paper cup was immersed into the melt and thereafter placed for a longer period in a drying chamber heated to 120° C. Thereafter, the paper cup was filled with a solution of dye stuff and exposed for an hour to the action of a stream of water vapor which was heated to 110° C. The mixture of hard paraffin and hydrogenated pentacyclopentadien was found to be completely impermeable at this temperature since no solution of dye stuff had leaked through the paper cup.

Example 8

A wax having a melting point of 102° C. was obtained by mixing 70 parts by weight of the hard paraffin used in Example 1 and 30 parts by weight of polyethylene having a molecular weight of approximately 13,000. This wax was very flexible and particularly well suited for the impregnation of paper, paper-board or textiles and for coating metal foils and metal sheet. Sheets of paper were immersed into the melt and then placed in a drying chamber heated to 130° C. where a part of the wax coating taken up was sweated off. Containers produced

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from the impregnated sheets of paper withstood temperatures of as high as 100° C.

We claim:

1. A sterilizable package for solid and liquid consumer goods comprising a base material defining the package and a surface coating of paraffin having a melting point of above 90° C., said coating additionally containing from 2-70% of a polymerization product having a melting point in excess of 100° C. and selected from the group consisting of polymerization products of cyclopentadien, dicyclopentadien and hydrogenated polymerization products of cyclopentadien and dicyclopentadien.

2. Sterilizable package according to claim 1, in which said coating contains from 5-20% of said polymerization product.

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3. Sterilizable package according to claim 1, in which said group member is refined.

4. Sterilizable package according to claim 1, in which said base material consists of paper material.

5. Sterilizable package according to claim 1, in which said coating is mixed with a material to increase the adhesiveness of said coating to a coated surface.

References Cited in the file of this patent

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