MOLDED PULP PRODUCT AND PROCESS

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This invention relates to molded pulp articles. More particularly it relates to molded pulp articles of high resistance to the penetration of oils, fats and greases over a wide temperature range and to the method of producing the same.

Articles molded of cellulosic fibers, and more particularly from papermaking fibers, can be made into attractive and inexpensive dishes and food containers. Moreover, it has been found that such articles be able to hold both hot and cold food without permitting penetration of the liquid content, both water and oils, of the foodstuff. However, the prior art has left much to be desired insofar as articles of this type which have good liquid penetration resistance, particularly resistance to the penetration of oils and fats over the entire temperature range at which most foods are served or stored. Attempts have been made in the prior art to render molded pulp articles resistant to the penetration of oils and fats at various temperatures but these have only met with limited success. For example, molded pulp articles treated with a low melting point wax or paraffin provide resistance to the penetration of oils or fats at room temperature or slightly above, but oils at temperatures of about 185°F or greater penetrate these articles almost immediately, making them unsatisfactory for holding hot foods or other hot oily substances.

On the other hand, molded pulp articles treated with a high melting wax (M.P. 195°F.) can be made resistant to the penetration of hot oils or fats at temperatures below 195°F., but these are found unsatisfactory for holding materials containing oils or fats at temperatures less than about 150°F. Various attempts to treat pulp articles with a mixture of low and high melting point waxes have not been successful because in such processes these waxes have been blended and merely result in a mixture having a melting point lying between the respective melting points of the two waxes making up the mixture.

The term "oil" will hereinafter be used to include oils of synthetic, mineral, vegetable and animal origin, greases, fats and the like, whether they are encountered in cooked foods or other substances.

It is an object of this invention to provide a molded pulp article which is resistant to the penetration of oils applied thereto over a wide temperature range. It is another object to provide a molded article of the character described which is also resistant to the penetration of other liquids, e.g., water. It is yet another object of this invention to provide an improved container of molded pulp which is capable of holding both hot and cold foods and preventing penetration of the oil or other liquid content thereof during its use. Still another object is to provide molded articles of the character described in which the penetration of oils above 195°F. can be controlled or prevented over an extended period of time. Another and important object of this invention is to provide a method of producing a molded cellulosic article which is resistant to the penetration of hot and cold oils. These and other objects will become more apparent upon considering the following description of the present invention.

The product of this invention may be described as a molded pulp product having substantially uniformly distributed therethrough from about 1% to about 16% by weight of a mixture of a first wax melting above about 212°F. and a second wax melting below about 165°F., the amount of said first wax in said mixture being in excess of that amount which is compatible with said second wax when said waxes are melted together and subsequently solidified.

As will be explained more fully hereinafter, the wax components are introduced into the molded article by incorporating the same into the fiber or pulp stock prior to the actual molding of the article. This is most conveniently accomplished by the use of emulsions or dispersions of the waxes.

The commonly used hydrocarbon waxes are known to be made up of a mixture of a large number of different hydrocarbon molecules varying in the number of carbon atoms contained. This in turn means that the various hydrocarbon waxes are compatible, and blends may be made to obtain a hydrocarbon wax having the desired melting point. In true wax blends essentially all of the blend melts at the same temperature, that temperature being intermediate between the melting points of the waxes going to make up the blend and determined by the percent and melting point of each of the waxes used in the blend. The use of two or more such compatible waxes which behave in this manner explains the inability of prior art processes to achieve the wide range of protection against oil penetration in molded pulp articles now achieved by the practice of this invention.

In contrast to the prior art, this invention requires the use of two waxes which have widely spread melting points and which exhibit a degree of incompatibility toward each other. This required degree of incompatibility is used to provide in the finished molded pulp article protection against oil penetration over a wide range defined as extending from essentially the lower temperature limit attainable by the low melting point wax when used alone up to the higher limit attainable by the high melting point wax when used alone. This desired protection is in turn due to the presence in the molded pulp article of waxes having a spread of melting points, there being present distinct phases of waxes substantially identical to the low melting wax, and the high melting wax and a spectrum of wax phases having melting points intermediate of the melting points of the two wax components.

Thus, there is achieved not only a wide range of temperature protection but also complete protection within this range.

The compatibility or incompatibility of waxes may be recognized optically or by plotting a solidification curve for a mixture of two or more waxes as they cool from a molten condition. If, for example, two waxes are incompatible, a plot of temperature against time will show two breaks in the curve, one of which occurs at approximately the melting point of the higher melting point wax, the other at the melting point of the lower melting point wax. A limited degree of incompatibility is evidenced by an intermediate break or breaks in the curve. These intermediate breaks in the cooling curve indicate that the heat of crystallization of a compatible compound is retarding the cooling rate. For example, in the prefered waxes used in the practice of this invention, it has been found that the greatest degree of compatibility is achieved when approximately 85% by weight of total wax is of the low melting component and 15% by weight of the high melting component. The performance of our finished molded pulp articles, in terms of their ability to furnish protection from oil penetration throughout the entire temperature range, demonstrates that there are a multiplicity of such compatible mixtures giving a multiplicity of waxes, each having a slightly different melting point. In addition, however, the finished pulp article also contains portions of the high melting point wax and of

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the low melting point wax in forms essentially identical to their original form.

The high melting point wax used in this invention is defined as one having a melting point above 212°F. Since temperature much in excess of 300°F would begin to degrade the molded pulp article itself, it is unnecessary to employ a high melting point wax having a melting point greater than 300°F. This high melting wax component may be further defined as one which exhibits the required degree of incompatibility to the low melting wax.

Among the high melting point waxes which are suitable for the practice of this invention, the preferred wax is Acrawax C (sold by Glyco Chemicals). Acrawax C is a complex of animal wax and has a melting point of about 284°F. It is understood to be essentially ethylene bis-stearamidic. Likewise, methylene bis-stearamidic and ethylene bis-stearamidic may be used as well as any other wax-like material conforming to the requirements given above. Among others, it is not considered available high melting point N,N'-ethylene bis-stearamidic waxes may be listed: Airwax 140 which has a melting point of 284°F (sold by Celgy Chemical Company) and Carlisle wax 280 which has a melting point of 280-290°F (sold by Carlisle Chemical Works, Inc.).

The low melting point wax component is one which has a melting point of 165°F or less but preferably not below about 50°F. The lower limit placed on the melting point of this low melting wax component is determined by the temperature of the oil against which this wax component is to protect the molded cellulose article. Under normal circumstances, for example, where the cellulose article is a food container, the lower temperature oils or fats will be at approximately room temperature. It would not, of course, be desirable to store or process water-penetrating oil or fats which melt at room temperature or below. This, therefore, indicates a practical lower limit of about 50°F for the low melting point wax component.

A variety of known low melting point waxes are suitable for the practice of this invention. Hydrocarbon waxes, the microcrystalline waxes, beeswax, and the like are suitable low melting point waxes.

If the cellulose article, treated in accordance with this invention, is to be exposed over prolonged periods to the atmosphere, or oxidative conditions, it is preferable that the low melting point wax component contain a minimum amount of liquid hydrocarbons, i.e., not more than about 15% by weight. Waxes which have liquid hydrocarbons below this level are obtainable, or they may be treated to remove these liquid components by means well known to those skilled in the art.

The amount of wax used should be that which will provide at least about 1% by total weight in the molded pulp article. Although a smaller amount of wax may be used with acceptable results, it is difficult to physically distribute less than about 1% uniformly throughout the fibers. It has been found economically practical to use more than about 15% by weight. The amount of high melting point wax in the wax mixture must be in excess of that amount which is compatible with the low melting point wax when the waxes are melted together and subsequently solidified.

The pulp used to form the molded article is prepared in accordance with known techniques which include formation of a water-fiber slurry. The waxes used in this invention may be added at any suitable point during the slurry formation, preferably to the beater stock.

Because of the very high melting point of the high melting point wax component, it is often difficult to form a suitable water emulsion for introducing it into the fiber stock. Therefore, the finely divided high melting point wax component is most conveniently formed into a water dispersion and added in this form to the slurry. Addition of the dispersion is preferably made to the stock in the beater. Of course, in those cases where an emulsion can be made with the high melting point wax component, it may be used in place of the dispersion.

In making a dispersion of the high melting point wax component to be added to the slurry, the high melting wax should be used in a finely divided particulate form, the particles having a maximum dimension not exceeding about 350 microns. If any substantial quantity of the high melting wax component comprises particles larger than 350 microns, there is a possibility of forming wax spoils in the line molded article and uniformity of resistance to oil penetration may not be achieved.

The low melting point wax component can easily be made up in the form of an oil-in-water emulsion and is conveniently introduced into the slurry in this form. However, other techniques are equally suitable. For example, the wax component may be chilled (with liquid nitrogen or any other suitable coolant), ground to the desired size and then introduced as a dispersion. As in the case of the higher melting wax component, the lower melting wax is preferably added to the stock at any time before formation. Addition to the beater stock has been found to be preferred in the practice of this invention.

In making emulsions of the low melting wax components, it is preferable to form an emulsion wherein the discontinuous phase (wax) particles range from about 2 to 5 microns in size. Although larger particles may be used, wax dispersions having the larger particles are often difficult to formulate.

The high melting and low melting point wax components may be conveniently introduced into the slurry as a single dispersion. This can be accomplished by preparing a dilute emulsion of the low melting point wax component and then dispersing the high melting point wax therein. An alternative method of introducing the wax components as a single preparation is to preblend them by melting and subsequent solidification before introduction into the slurry. A combination of these methods may also be used, of course.

The methods used in forming a molded cellulose article are well known to those skilled in the art. U.S. Patents 2,017,017, 2,237,573 and 2,752,830 are examples of apparatus suitable for forming and drying the articles of the present invention. The drying operation may also be accomplished by the use of conventional tunnel drying, i.e., without the application of pressure.

Additional additives or treating agents may be added to the slurry to impart other desirable characteristics to the finished molded pulp article of the present invention. As an example, agents such as rosins or modified rosins may be added to decrease the penetration of aqueous liquids. When these are added, it is usually desirable to exhaust the rosins onto the fibers by well known methods, e.g., to lower the pH of the slurry by adding a material such as papermaker's alum. The rosins or modified rosins may be exhausted onto the fibers in the slurry before or after the wax components of this invention are added and they are generally present in concentrations up to about 2.5% by weight of the molded article.

It is also within the scope of this invention to add other treating agents, such as finely divided particulate matter, to increase the surface area and thereby improve wax retention, improve strength or modify other physical properties of the finished molded article. For example, finely divided silicates may be introduced onto the fibers to increase the surface area and to impart strength to the article. This is illustrated by Example VI hereinafter.

Such finely divided material should be of such a particle size that its surface area is not greater, and preferably less than that of the fibers making up the cellulose article. If it is used to enhance resistance to oil penetration through increased surface area, it should be an oleophilic material, i.e., it should be wetted by oils.
Finally, it is, of course, possible to add pigments or dyestuffs to give the article any desired color. The invention may be further described by the following examples, which are meant to be illustrative and not limiting.

**Example I**

A furnish was prepared by charging a pulp beater with ground wood and unbleached sulfate pulp. The quantities used were such as to provide, on a bone-dry basis, 97.5% ground wood and 7.5% by weight unbleached sulfate. The consistency of the furnish was made up to approximately 5% and it was beaten until a Canadian freeness of approximately 200 was achieved.

Neutral rosin size was added to the beater and thoroughly dispersed. The quantity of rosin present was equivalent to about 1% by weight of the fibers. After the rosin had been thoroughly dispersed, a solution of papermaker's alum was added to the beater in an amount sufficient to reduce the pH of the furnish to between 4.1 and 4.5.

In separate operations, a dispersion of Acracowax C and an emulsion of Aristowax were made up. The Acracowax C had a melting point of 284°F, a flash point of 545°F, and may be further characterized as a complex nitrogen derivative of higher fatty acids. The Aristowax had a melting point of 160 to 165°F, and was a hydrocarbon paraffin wax.

In preparing the Acracowax dispersion, 1.6 grams of stearic acid was melted and added to 1.2 grams of monooctanoletheramine, together with 2.2 grams of water, while the temperature was maintained between 70 and 75°C. After a period of about 5 to 10 minutes, 60 grams of water heated to 70 to 75°C was added. To the resulting mixture, were then added 3 grams of isopropanol and finally 32 grams of Acracowax ranging between 5 and 100 microns in size. The dispersion was stirred until it had cooled to approximately room temperature.

The emulsion of the lower melting point Aristowax was made by melting 22 grams of Aristowax with 1.81 grams of stearic acid. The mixture was then brought to a temperature of about 205 to 210°F. To this were added 0.38 gram of monooctanoletheramine and 1.2 grams of water. Finally, an additional 74.6 grams of water, heated to boiling, was added with rapid stirring to form an oil-in-water emulsion.

A quantity of the Acracowax C dispersion prepared as described above was then added to the beater in an amount sufficient to provide the equivalent of 1.5% by weight Acracowax C on the dry weight of the fibers. Following the addition of the higher melting point wax, a portion of the emulsion of the Aristowax was added to the furnish in the beater in an amount to provide 0.5% by weight of the fibers, resulting in the inclusion of 2% total wax by fiber weight. The furnish was then pumped to a slurry pit and diluted to a consistency of approximately 1%. Molded pulp plates were then prepared by the process described in U.S. Patent 2,017,017, the temperatures of the drying dying grading from 100 to 500°F.

In order to evaluate the ability of the resulting plates to resist penetration by cold and hot oils, corn oil at 35° F. and at 240° F. was poured into plates made in accordance with this example. It required two hours for the cold oil and 24 hours for the hot oil to penetrate through the plates to the bottom where the oil was visibly present. In actual use these plates are suitable for resisting penetration of oil over a temperature range from 35°F to 320°F.

In contrast to the performance exhibited by the plates prepared in accordance with this example, one plate prepared by standard procedures containing wax melting at 165°F. permitted the corn oil at 35°F. as well as the corn oil at 165°F. to penetrate in two minutes.

**Example II**

A furnish was prepared as in Example I to the point where the rosin of that example was added. In place of the rosin of Example I a maleic anhydride modified rosin (sold as Pexol by Hercules Powder Company) was added to the beater to furnish sufficient of this modified rosin to equal 2% of the dry weight of the fibers. Alum was then added to reduce the pH to between 4.1 and 4.5. An Acracowax C dispersion and an Aristowax C emulsion were then added as in Example I above and molded plates were prepared from the furnish. The resulting plates gave oil resistance comparable to that described in Example I.

**Example III**

Plates were prepared from a furnish identical with that of Example I except that a small quantity of green MX (Calco Chemical Co.) was added as a dyestuff. This dyestuff is intended to be malachite green. The resulting plates were a pleasant green and possessed the same ability to resist penetration of oil as the plates of Example I.

**Example IV**

A furnish was prepared as in Example I except that a sufficient quantity of the Acracowax C dispersion was added to provide 12.0% by fiber weight and enough Aristowax C emulsion was added to provide 4.0% by fiber weight, giving a total wax content of 16.0% by weight of dry fibers.

The rate of cold and hot corn oil penetration for the plates prepared from this furnish was greater than 24 hours for corn oil at 240°F. and greater than two hours for corn oil at 72°F.

**Example V**

A furnish like that described in Example I was prepared except that pure ethylene bis-(stearamide) (melting point 284°F.) was used in place of the Acracowax C and was added in an amount equivalent to 2.0% by weight of the fiber and a hydrocarbon paraffin wax, melting between 150-155°F. was substituted for the Aristowax of that example and in an amount equivalent to 0.5% by weight of the fiber. When plates were prepared from this furnish, the results were distinguishable from those of Example I in that the penetration of corn oil at an initial temperature of 240°F. took more than 24 hours; while corn oil at 72°F. penetrated the plate in somewhat less than two hours.

**Example VI**

To the furnish prepared in accordance with Example I above was added quantity of sodium silicate solution equivalent to about 7.5% based on the dry weight of the fiber. When plates were molded from this furnish, the strength of the plate was greatly increased, while the oil resistance showed improvement over the product of Example I in that it required more than 24 hours for corn oil at 240°F. and more than 2 hours for corn oil at 35°F. to penetrate.

**Example VII**

Plates were prepared from a furnish as in Example I in which the low melting Aristowax was replaced with an equivalent weight of microcrystalline wax having a melting point of 155°F. The resulting plates exhibited approximately the same degree of resistance to penetration as those prepared in Example I. Likewise when the Aristowax was substituted with an equivalent weight of paraffin having a melting point of 128°F. the resulting paper plates showed the same good resistance to the penetration of corn oil.

However, when the Aristowax was replaced with an equivalent amount of microcrystalline wax having a melting point between 190 and 195°F. (i.e., above the 165°F. specified), the resulting paper plates did not exhibit resistance to the penetration of the cold oil as in the case of Example I.

The process of this application is applicable to making molded cellulosic articles from mechanical pulp as
illustrated in Examples I through VII and from chemical pulp as illustrated in the following Example VIII. Moreover, the process is also, of course, applicable to treating so-called semichemical pulp.

Example VIII

A furnish having a consistency of about 5% was prepared using all bleached hard wood kraft pulp and containing 2% by fiber weight of Pexol (a maleic anhydride modified resin). The furnish was transferred to a Dynapulper where it was defibered. To the resulting dispersion was added a sufficient amount of alum to give a final pH of 4.1 to 4.5. The furnish was then run through a Jordan to give a Canadian standard freeness of 300 to 325. To this was added an Acrawax dispersion prepared as in Example I and an Aristowax emulsion prepared as in that example. The higher melting point wax component was added in an amount sufficient to furnish 1.5% by fiber weight while the lower melting component was added in an amount sufficient to furnish 0.5% by weight of the fiber. The total amount of wax added was therefore equivalent to 2% of the fiber weight. The furnish was then diluted to a consistency of 1% and paper plates were prepared therefrom as in Example I. The resulting plates when exposed to corn oil at 35° F. and at 240° F. exhibited a performance identical to that of the plates of Example I.

Example IX

The Aristowax used in Example I as the low melting wax component was treated to remove substantially all of the liquid hydrocarbon constituents contained therein. This was done by subjecting the wax to successive treatments with methyl ethyl ketone. The wax was dissolved in the solvent at a temperature equal to the boiling point of the solvent and the resulting solution was cooled to about 80° F. The wax which precipitated was filtered off and was retreated by this method three more times. At the end of these four successive treatments the liquid hydrocarbon constituents had been reduced to 0.05% by weight of the wax. The treated Aristowax was then used in forming paper plates by the process described in Example I and by using the same quantities as given in that example. The resulting plates were evaluated for their ability to resist penetration of cold corn oil at 35° F. after being exposed to air for various periods of time. The results of these tests indicate that the plates made in this example can be stored for times considerably in excess of one year while still maintaining their excellent resistance to the penetration of cold oils.

We claim:
1. A molded pulp product having substantially uniformly distributed therethrough from about 1% to about 16% by weight of a mixture of a first wax melting above about 212° F. and a second wax melting below about 165° F., the amount of said first wax in said mixture being in excess of that amount which is compatible in the solid state with said second wax when said waxes are melted together and subsequently solidified and said mixture being present in said product as discrete wax phases of varying wax composition.
2. The molded pulp product of claim 1 including a surface area increasing amount of finely divided particulate matter substantially uniformly distributed therethrough.
3. A molded pulp product having substantially uniformly distributed therethrough from about 1% to about 16% by weight of a mixture of a first wax melting above about 212° F. and a second wax melting below about 165° F., said first and second waxes exhibiting toward each other a degree of incompatibility in solid form and being present in said mixture in a ratio such that after melting and subsequent solidification there are a plurality of discrete wax phases present, one phase being substantially identical to said first wax, another phase being substantially identical to said second wax and a third phase being a homogeneous mixture of said waxes having a melting point intermediate the melting points of said first and second waxes.
4. A molded pulp product having substantially uniformly distributed therethrough from about 1% to about 16% by weight of a mixture of a first wax melting above about 212° F. and a second wax melting below about 165° F., said first and said second waxes exhibiting toward each other a degree of incompatibility in solid form and being present in said mixture in a ratio such that after melting and subsequent solidification there are a plurality of discrete wax phases present, one phase being substantially identical to said first wax, another phase being substantially identical to said second wax and a plurality of wax blend phases which exhibit a melting point range from substantially that of said second wax to substantially that of said first wax.
5. The process comprising the steps of forming an aqueous slurry of pulp fibers, introducing into said slurry a mixture of a first wax having a melting point above 212° F. and a second wax having a melting point below 165° F., depositing pulp fibers including said waxes in the form of a structural shape on a mold, and drying resulting structural shape at a temperature above the melting point of said first wax, said first and said second waxes exhibiting toward each other a degree of incompatibility in solid form and being present in said mixture in a ratio such that after melting and subsequent solidification there are a plurality of discrete wax phases present, one phase being substantially identical to said first wax, another phase being substantially identical to said second wax and a third phase being a homogeneous mixture of said waxes having a melting point intermediate the melting points of said first and second waxes.

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