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COATED PAPER AND PAPER PRODUCTS

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This invention relates to the coating of paper and paper products, and includes novel methods for coating or sizing paper and paper products to render same resistant or impervious to fats, oils, organic solvents, emulsions, and water; and novel paper and paper products suitable for wrapping purposes, and for making cartons and receptacles for holding milk, salad dressing, fruit juices, butter, cake, and other food products.

The present application is a continuation of my copending application Serial No. 217,309, filed July 2, 1938, on Coated paper and paper products.

To avoid repetition I hereinafter intend to include under the term "paper" any kind of paper or paper products which it may be desired to coat and render impervious to fats, etc., as above referred to. Also by the words "coated" or "coating" I intend to include not merely a surface film but a more or less impregnation of the paper by the alginate.

One object of the invention is to coat paper with a water soluble alginate which will form a flexible film and render the paper resistant to waxes, oils, and organic solvents.

Another object is to apply to paper coated as above, a second coating of wax, oil, lacquer paint, resin, alginate or other film or coating. The second coating or film if of wax and the like renders the paper resistant to water, emulsions and water solutions; if of resin, the second coating renders the paper resistant to fats, oils, emulsions and water.

In some cases for the first coating a solution of double alginate salts may be used, as such salts render the paper impervious or resistant to water, as well as organic solvents, oils and fats.

In some cases the paper coated with double alginate salts as above may be treated with a second coating of wax resins, etc., as above stated.

Heretofore so-called moisture-proof or oil-proof paper has usually been coated with a film of resin or wax. Such films, however, usually crack where the paper is folded or creased, and consequently such paper is not satisfactory for use in the manufacture of paper containers. Further, such paper usually has a number of small incompletely impregnated portions which have rendered many cartons made from such paper useless. Further, in such paper an excess of resin or wax coating solutions is absorbed rendering such paper expensive.

I have found that by applying an alginate solution to paper, and then drying it, and then

applying a second coating as aforesaid, an appreciably smaller quantity of the second coating material is required to make the paper water-, grease-, or oil-proof. Also that when paper is first coated with an alginate as above described, resinous coats thereafter applied do not crack when the paper is creased or folded.

One practical method of coating the paper with alginate is as follows:

(1) Sufficient sodium alginate is dissolved in water to form a 2% solution of the alginate having a Woolwich viscosity of about 100 seconds (which is the time for a steel ball $\frac{1}{4}$ " in diameter to fall 15 cm. through the solution at 20 degrees C.). Said solution also has a pH of around about 7. In making such solution I preferably use alginates manufactured as set forth in U. S. Patents #1,814,981, #2,036,922 and #2,036,934. The aforesaid alginate solution is preferably sprayed onto the sheets of paper and then dried. The alginate solution may be applied to dry or to moist paper. The alginate forms a thin film on the paper and renders it resistant to waxes, oils and organic solvents.

Instead of spraying the alginate solution may be applied to the paper in other ways, and under various degrees of temperature, pressure and suction. Applying the alginate solution under pressure will give enhanced penetration. Also if the solution is heated increased penetration and weight of film is obtained.

(2) Paper coated as aforesaid may be further coated with wax, resin, etc. For instance, a solution of "Vinylite" (which is a polymer of several of the vinyl $\text{CH}_2\text{:CH}$ compounds) may be sprayed on the paper coated with the alginate. For comparison and to demonstrate the efficiency of the alginate coating, a piece of paper not treated with the alginate was coated with "Vinylite," and it was found that the alginate coated paper had two grams of resin per square foot on it, whereas the untreated paper had $2\frac{1}{2}$ grams per square foot; also the resin on the alginate coated paper was on the surface, whereas the resin on the untreated paper had penetrated into the paper. When the papers were bent to form boxes the resin on the paper coated with the alginate did not crack; but the resin on the untreated paper cracked. Also oil poured into containers formed respectively out of the alginated coated paper, and of the untreated paper seeped through cracks in the containers formed of the untreated paper; but did not seep through the containers formed of paper treated with the alginate.

When the paper is for a commercial use, a second coating will cover up any imperfections which might possibly be found in the first coating, and will render the paper entirely resistant to penetration of oils, fats, organic solvents, etc.

The waxes may be applied by first dissolving in a volatile organic solvent and then spraying, dipping or brushing such solution onto the paper. Mastic, copal, benzoin, shellac, colophony, damar, sandarac, and anime, and the so-called true or natural resins may be used. Synthetic resin, made by the action of a resinifying agent or non-resinous substance, including the phenol-formaldehyde products, cumaron resin, glycerol and phthalic acid condensation bodies, ketone resins, polymerization products of vinyl compounds, urea and thiourea derivatives of the sulfur-phenol resins may be used. Also resins made by the action of chemical agents on natural resins, more especially rosin or colophony, resulting in a substantial modification of composition and properties.

(3) Another practical method is as follows:—

A 2% water solution of sodium alginate, having a Woolwich viscosity of 100 seconds can be applied to the paper in a reverse roll paper coating machine, the paper being fed between the usual rolls and in its passage coated with the solution, and the coated paper passed through a drier heated to 200° F. The paper may be passed through such a machine at a rate of 37 feet per minute. After the paper is coated on one side and dried, it is reversed and run through a second time, so that both sides of the paper are coated with the alginate solution. The coating would be about .003 inch thick and 30½ pounds of the solution suffice for coating 1380 square feet of paper on both sides. This is equivalent to about 0.25 pound of sodium alginate per thousand square feet of paper surface covered. The paper thus coated is impervious to oil, and could be used for containers holding oils and fats. All standard types of paper coating machines may be used for applying the coatings.

(4) Bottles made from paper coated as in section (3) were dipped in a 180° solution of paraffin for one-half minute, removed and dried, and when such bottles were compared with similar bottles formed of paper not coated with alginate, but dipped in the same paraffin solution, it was found that bottles made from paper coated with alginate absorbed an appreciably smaller amount of paraffin, which would result in saving thousands of dollars per year in manufacture of bottles in quantities. Furthermore, a large number of bottles not treated with the alginate had cracks in films and imperfect coatings rendering them useless for the desired purpose.

(5) An example of coating light paper with alginate follows: A 1% solution of sodium alginate in water, having a Woolwich viscosity of 2 seconds, was applied to light weight paper by a reverse roll paper coating machine, in the manner above described. The paper so coated is flexible and the alginate coating or sizing does not crack when the paper is bent. This treatment also gives a good finish to the paper and inks, paints and printing compounds may be applied thereto.

(6) A second coating of alginate may be applied to the paper treated as in section (5) after the first coating has dried. The second coating may be a more viscous solution and of higher concentration; such as a 3% solution of sodium alginate having a Woolwich viscosity of approxi-

mately 50 seconds; and this will form a thicker film on the paper.

(7) Instead of sodium alginate a copper-ammonium alginate may be used. In one instance 10 pounds of 5% paste of copper alginate, and ½# of cupric hydroxide dissolved in 3# of ammonium hydroxide solution was mixed with water to form a 1% solution. This solution was applied to the paper in the manner above described for sodium alginate solutions. The treated paper was resistant to water and emulsions. Non-edible alginate salts may be used on paper intended for use for packaging greases, lubricating oils, soaps, and building paper; but should not be used on paper for packaging foods.

(8) A specific example of coating paper pulp containers with alginates is as follows: Paper containers were molded into various shapes including bottles, for holding emulsions, oils, water, etc. A 2% solution of sodium alginate having a Woolwich viscosity of 7 seconds was heated to 120° F. and poured into the dry containers, and allowed to stand therein for several minutes and then removed. The containers were then dried, and melted paraffin poured into them, and they were agitated so that all treated surfaces were covered by the paraffin. The alginate coating prevented the paraffin penetrating through the containers, so that their exterior appearance was clean and uniform. When the hot paraffin was applied as above to paper containers not coated with alginate it seeped entirely through the containers, giving them a very undesirable exterior appearance. Containers having the alginate and wax treatment were filled with water but there was no seepage, the containers being completely water-tight. In the above instance the sodium alginate used contained about 10% cellulose of the type normally found in the kelp from which the alginate is made.

In place of paraffin wax, other waxes, including cerecine, carnauba, candelilla, beeswax, montan, spermaceti, bayberry wax, stearine and Japan wax may be used. Such waxes are heated to their own normal melting points before being applied.

Numerous other examples of the use of alginates in the coating or sizing of paper, with subsequent treatment with wax or resins, etc., could be given, but the foregoing examples are sufficient to enable others familiar with the art to understand and use the invention.

I have found that alginates containing some cellulose or filler will give a continuous slightly rough surface to which the resin and wax films readily adhere. The cellulose might be that originally found in the kelp from which the alginate is extracted, or some other type that is added, and I have also found that in some cases an inert filler, such as diatomaceous earth, clay, etc. may be used. Various alginate salts may be used, such as potassium alginate, ammonium alginate, triethanolamine alginate, aliphatic amine alginate, substituted aliphatic amine alginates including chlorinated ethanolamine alginate, and sodium phospho-alginate. Also alginates containing ingredients to aid in their solution (such as disclosed in U. S. Patent #2,000,807).

Some double alginate salts may be used, such as cupric-ammonium alginate, zinc-ammonium alginate, cupric-triethanolamine alginate, aluminum-triethanolamine alginate, aluminum-butanolamine alginate, zinc-chlorinated-butanolamine alginate, tin-triethanolamine algi-

nate, and similar double alginate salts. The film produced by triethanolamine alginate salts and double triethanolamine alginate salts is very flexible. Such double alginate salts may be made by adding to ammonium alginate solution an excess of ammonia and a soluble salt, such as cupric hydroxide, cupric sulphate, zinc sulphate, etc. depending on the salt desired. Other methods of obtaining double salts of alkali-earth metals, metals, and alginates also may be used but the examples given are sufficient. When such a solution is used, it will form an insoluble alginate film. The double alginate salts may be used either alone as a size or first coating or as a second coating over a primary alginate coating.

The paper which may be treated includes papers used in printing, thin papers used as wrappers, molded paper pulps, card boards for making containers and boxes, etc. There is no restriction on the type of paper which may be used.

I do not consider my invention limited to the foregoing examples. The alginate solutions may be made up of various concentrations, but I have found that usually between $\frac{1}{2}\%$ and 3% is a good working range. Alginates vary considerably in viscosity, from those having extremely low Woolwich viscosities in a 2% solution (such as described in U. S. Patent #1,814,981), to those having extremely high viscosity, as those described in U. S. Patents #2,036,922, #2,036,934, #2,097,224, #2,097,225, #2,097,228 and Bennett Preble's applications, Serial No. 46,213, filed October 22, 1935, for Amine alginate product and process, Patent No. 2,158,486, and Serial No. 46,214, filed October 22, 1935, for Triethanolamine alginate product and process, Patent No. 2,158,487. By using alginates of varying viscosities and of varying concentrations, varying desired degrees of penetration, thickness and weight of film formation may be obtained. Alginates which have a higher viscosity for a given concentration can usually be used in a more dilute form. Alginates having a very low viscosity can be used in a more concentrated form. The degree of concentration may be used to control the speed of wet-

ting with the alginate solution; and ordinarily the lower the viscosity of the solution used the greater will be the wetting speed.

I have found that very viscous solutions or high concentrations of alginate do not satisfactorily wet or penetrate the paper, and do not give a very satisfactory and uniform coating.

I claim:

1. The method of treating paper for containers, wrappers, and the like, consisting in applying thereto a primary coating comprising an aqueous solution of substantially 1% water soluble alginate having a Woolwich viscosity of about 2 seconds, drying said coating, applying a second coating comprising an aqueous solution of substantially 3% water soluble alginate having a Woolwich viscosity of about 50 seconds, to render the paper resistant to waxes, oils, and organic solvents; drying said second coating; and applying thereover an outer coating of a solution taken from the group consisting of resins and waxes.

2. The method as set forth in claim 1, in which one alginate coating contains a cellulose filler.

3. The method as set forth in claim 1, in which one alginate coating contains an inert earth filler.

4. The method as set forth in claim 1, in which one alginate coating consists of double alginate salts.

5. Paper for containers, wrappers, and the like having a primary coating of water soluble alginate having a Woolwich viscosity of about 2 seconds, and a second coating of water soluble alginate having a Woolwich viscosity of about 50 seconds, to render the paper resistant to waxes, oils, and organic solvents; and an outer coating thereover taken from the group consisting of resins and waxes.

6. Paper as set forth in claim 5, in which one alginate coating contains a cellulose filler.

7. Paper as set forth in claim 5, in which one alginate coating contains an inert earth filler.

8. Paper as set forth in claim 5, in which one alginate coating consists of double alginate salts.

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