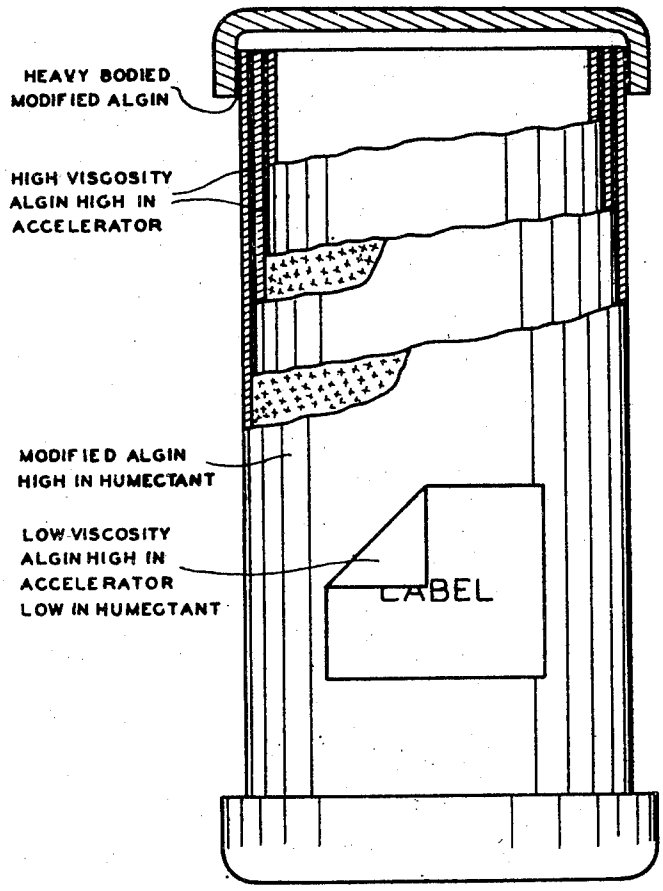
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FILM-FORMING COMPOSITIONS FOR OIL-PROOF CONTAINERS

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FILM-FORMING COMPOSITIONS FOR OIL-PROOF CONTAINERS

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This invention pertains to the preparation of compositions, consisting primarily of algins, which on spreading and drying yield oil-proof, highly adhesive and flexible films, and to the use of such compositions in the manufacture of laminated papers and of paper containers for oils and greases.

A purpose of the invention is to provide means for working paper stock into containers which are wholly proof against leakage of or staining by oleaginous contents and which maintain the oil-proof characteristic through extended storage of the filled container and also when it is subjected to rough handling.

A purpose of the invention is to provide materials for producing a laminated paper which is at once highly flexible and completely and permanently grease-proof and which may be used for wrapping cheese, butter and other oily or greasy products.

A purpose of the invention is to so modify the normal characteristics of an algin film as to improve its stability and to cause it to remain flexible for an indefinite period, even under conditions of varying humidity.

A purpose of the invention is to so modify the normal characteristics of an algin film as materially to increase its adhesive property and to cause this property to develop rapidly after spreading.

The paper containers to which the invention most specifically applies are of two general types: cylindrical and rectangular. The first named are generally used for liquids and soft or semi-solids, as for example, lubricating oils and greases, ointments and the like. Such solids as cheese, butter and oleomargarine are more often placed in rectangular, folded containers.

Cylindrical containers are made, in general terms, by forming on a shaft or mandrel a tube consisting of a plurality of plies of suitable paper, wound in spiral or convolute form and cemented together as wound. This tube is cut into lengths and paper or metal caps applied to close the ends. Paper caps are desirably used for relatively light materials and for small packages. Such heavy liquids as mixed paints may require metal caps, which are preferably applied with a special composition (see Example 6).

The attached drawing illustrates, in elevation and partial section, a three-ply cylindrical container made up with the compositions herein described, the thicknesses of the various layers being grossly exaggerated.

Rectangular containers may be made by folding laminated or previously coated paper or cardboard into the desired form and cementing the laps. They may also be made by folding up and cementing single-ply, uncoated paper and spraying or flooding with the described coating compositions.

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Either the cylindrical or the rectangular form may have a surface coating of one of the compositions applied either inside or outside, or both, though such coatings are more often given to cylindrical than to rectangular containers. Either type may have a label or labels affixed before or after sealing, for which purpose a specific modification of the invention is provided (see Example 3).

These methods of manufacture are well known and understood. They are mentioned here only because the different situations in which the compositions of the invention are used require the development of different properties or, more accurately, of the characteristic properties in different degrees.

The basic requirements in a composition adapted to the manufacture of an oil-proof paper package are as follows:

1. The composition must spread readily and form a homogeneous and consistent film, free from imperfections;

2. The film so formed, when dried to equilibrium with the atmosphere, must be wholly unaffected by contact with oils or fats, and impenetrable toward such substances;

3. The oil-proof pellicle formed by such drying must be strongly bonded to the adjacent paper surface or surfaces: i. e., the composition must be strongly adhesive;

4. The adhesive property or so-called "tack," which is substantially absent from the freshly spread film, must develop as rapidly as possible, by evaporation, on exposure of the film to the air: this characteristic is particularly important in the use of the composition for cementing tube plies, as it largely determines the speed at which the machine may be operated;

5. The dried pellicle must be to the greatest degree flexible in order to resist cracking when the sheet is folded or the package is deformed by rough handling;

6. The pellicle must come to equilibrium with even dry air at such degree of hydration as fully to retain its flexibility: it must not dry out and thereby become brittle.

The compositions herein described have three essential components, viz.: a film-forming material, which yields the oil-proof pellicle; an adhesion accelerator, and a humectant, together with water as a solvent and vehicle.

As film-forming agents, some of the alginates have an unique value. This is due primarily to their colloidal state, which causes them to filter out of the aqueous vehicle and form a pellicle on the surface of an absorptive material such as paper. As these substances do not penetrate the fibrous sheet to any material extent, a consist-

ent and impervious film may be very thin, and thus a small quantity of this moderately costly substance covers a relatively large surface. The pellicle, even when very thin, is to the last degree oil-resistant and, if maintained in a suitable state of hydration, is extremely flexible and difficult to rupture by handling or folding of the sheet on which it is deposited.

The prior art has recognized these advantages in describing the use of various alginates for the coating of paper and the lining of paper containers. But as such applications have not come into commercial use it would appear that the prior art did not recognize the inherent defects of the alginates. These defects, which are sufficient to destroy the utility of the unmodified alginates for these purposes, are: the slowness with which the freshly prepared film becomes tacky; the lack of sufficient bond between the pellicle and the paper surface on which it is spread, which in turn is due to the lack of penetration of the alginate into the capillaries of the paper, and the marked tendency of the unmodified alginate to dry out and become brittle.

The adhesion accelerator, of which glucose is an example, remedies the first of these defects by rapidly developing sufficient tack to provide initial adhesion, thus speeding up all cementing operations. It remedies the second defect by penetrating the fibre of the paper and thus providing the otherwise lacking bond between the alginate pellicle and the surface or surfaces of paper on which it is formed.

The humectant, of which sorbitol is an example, remedies the third defect by retaining in the pellicle sufficient water to render it permanently flexible. It also offsets a tendency, which may otherwise develop, toward crystallization of the adhesion accelerator in the pellicle and the consequent disturbance of the continuity of the oil-proof film.

Not all the alginates are suited to this use, only those which are freely water-soluble being available. Of the soluble compounds, the double salts or complexes of alginic acid with ammonia or amines and the heavy metals are barred by reason of their poor film-forming quality and, in most cases, by toxicity which renders them incompatible with any edible product. The amine and alkylolamine salts are functional but undesirable, partly by reason of their relatively high cost without any compensating advantage, partly because they cannot be prepared and shipped in the dry form.

The algins contemplated for the purpose of this invention are therefore limited (with the exception just made) to the salts of alginic acid with sodium and potassium (and the rare alkali metals which, again, are impracticable because of their cost) and with ammonium and magnesium. The sodium salt is preferred as being the least expensive and fully functional.

The viscosity of algin solutions of equal concentration varies over a wide range, depending on the method of manufacture and the extent to which the extremely large molecule of the alginic acid has been depolymerized in separating it from the algae in which it originates. It is preferable to use an algin having a moderately low viscosity, as for example a grade having a McMichael viscosity of 7500 centipoises in 4% aqueous solution. It is possible, however, to use algins having 4% viscosities ranging from about 250 centipoises to about 600 poises, controlling the viscosity of the composition as prepared for use by varying the degree of dilution. The range of viscosity here given is intended to be suggestive, not limiting, as algins outside this viscosity range may be employed for special purposes.

The specific viscosity of the algin used should be selected with a view to balancing the spreading property against film impenetrability. In order to spread readily by the methods currently used—brushing, spraying, glue-pot or doctor blade—the composition as diluted for use should have a mucilaginous consistency. For the coating of containers by bathing and draining a thinner dilution may be advisable. Such consistency as is required by the particular operation may be obtained by the use of a high viscosity algin, highly diluted, or of an algin of lower viscosity in greater concentration.

The first alternative is economical of algin, less of the solid being required to produce any desired spreading consistency. On the other hand, a thinner film is formed and, if dilution be carried too far, the algin will penetrate into the fibre of the paper instead of remaining on its surface and the film may lack tightness or may not be formed.

The second alternative yields a relatively thick dried pellicle, which is more certain to be oil-tight, but if the specific viscosity of the algin be too low and the concentration correspondingly high, the consumption of the most expensive ingredient of the composition will be excessive. The technical advantage, therefore, lies with the use of a relatively large quantity of a low viscosity algin, the economic advantage with the substitution of a smaller quantity of an algin of high specific viscosity.

It will be borne in mind, in considering the practical formulae given in the examples below, that the relatively small proportion of algin is the sole film-forming ingredient, and also the component which imparts substantially all the observed viscosity to the liquid composition and the oil-proof character to the dried film. The film thickness and the spreading properties of the composition are therefore governed, not by the weight relation of algin to other solids, but rather by the relation of algin to water; i. e., on the concentration of algin in the solution and on the specific viscosity of the algin. The adhesion accelerator and the humectant, while they strongly modify the characteristics of the algin pellicle, have only a slight effect on the thickness of the film or on those properties of the composition which affect its application.

In lieu of glucose as an adhesion accelerator one may use another sugar such as sucrose, dextrose or levulose, or a solubilized starch such as dextrin or amylodextrin. The glues and gelatines are not suitable substitutes in spite of the strong adhesiveness which some of them develop. In using any of these substances the equivalent weight is about eight-tenths that required in the use of an 80% glucose.

In lieu of sorbitol as the humectant one may use any of the polyhydric alcohols, such as glycerine or one of the glycols. It is preferable to use sorbitol or other humectant having an inherent humidity range, in spite of a possibly larger quantity required, as in the use of the alcohols the dosage must be carefully limited to avoid excessive hygroscopicity of the pellicle. This is particularly important in compositions used for exterior coatings, in which an excessive use of ethylene glycol or glycerol may render the composition permanently sticky.

It will be remembered that the purpose of the humectant is not to impart plasticity, per se, but rather to retain in the algin film that small but very necessary proportion of water by which the algin is maintained in a plastic and flexible condition.

The proportions in which the above components may be used are illustrated, but not limited, in the following examples of compositions which have been used with success in the large scale manufacture of cylindrical containers, ranging in size from one ounce to five gallons capacity. The algin used throughout had a McMichael viscosity in 4% aqueous solution of 7500 centipoises and the proportions given are by weight.

Example 1

Sodium alginate	parts	8
Glucose	do	46
Sorbitol	do	46
Water	do	100
Concentration algin in water	per cent	8
Ratio algin to total solids		1:12.5
Ratio algin to accelerator		1: 5.7
Ratio algin to humectant		1: 5.7
Ratio accelerator to humectant		1: 1.0

This example yields an all-purpose product generally adapted to the operations connected with manufacture of oil-proof cartons of different types, but is not so economical for some specific uses as other formulae given below. It affords a relatively thick and completely oil-proof pellicle with a high degree of stability, but develops its initial adhesion more slowly than the composition following.

Example 2

Sodium alginate	parts	4
Glucose	do	88
Sorbitol	do	8
Water	do	50
Concentration algin in water	per cent	8
Ratio algin to total solids		1:25.0
Ratio algin to accelerator		1:22.0
Ratio algin to humectant		1: 2.0
Ratio accelerator to humectant		11: 1.0

This product is specifically adapted to cementing the plies of paper tubes from which cylindrical containers are formed. The concentration of algin is high enough to give a relatively thick bonding and oil-proofing pellicle. The development of adhesion is promoted by largely increasing the proportion of accelerator at the expense of the humectant. Because of the protection afforded by the superimposition of plies, the requirement for humectant is at the minimum.

Example 3

Sodium alginate	parts	4
Glucose	do	88
Sorbitol	do	8
Water	do	100
Concentration of algin in water	per cent	4
Ratio algin to total solids		1:25.0
Ratio algin to accelerator		1:22.0
Ratio algin to humectant		1: 2.0
Ratio accelerator to humectant		11: 1.0

This is the same formula as in Example 2 but with double the quantity of water to reduce viscosity and facilitate brush spreading. The adhesion characteristic is exaggerated and the product is particularly adapted to the labelling of containers, either before or after filling.

Example 4

Sodium alginate	parts	7
Glucose	do	78
Sorbitol	do	15
Water	do	167
Concentration algin in water	per cent	4.2
Ratio algin to total solids		1:14.3
Ratio algin to accelerator		1:11.1
Ratio algin to humectant		1:2.1
Ratio accelerator to humectant		5.2:1.0

This product is specifically adapted to flooding the interiors of containers or for application as an exterior coating by spraying and draining. The relatively large proportion of humectant protects these exposed films from becoming brittle.

Example 5

Sodium alginate	parts	4
Glucose	do	96
Water	do	100
Concentration algin in water	per cent	4
Ratio algin to accelerator		1:24.0

This is a very free spreading product adapted solely to the labelling of small packages which are otherwise oil-proofed. It is strictly an adhesive, of very high grade, and should not be used for oil-proofing because of the lack of permanent flexibility which follows the omission of the humectant.

Example 6

Sodium alginate	parts	4
Glucose	do	77
Sorbitol	do	19
Water	do	60
Concentration algin in water	per cent	6.7
Ratio algin to total solids		1:25.0
Ratio algin to accelerator		1:19.2
Ratio algin to humectant		1:4.7
Ratio accelerator to humectant		4:1.0

This is a heavy bodied composition adapted specifically to cementing caps onto cylindrical containers.

To each of the above formulae it is desirable to add a minute amount of a nontoxic and odorless preservative such as n-butyl-p-hydroxybenzoate at a concentration of about 0.05% by weight of the composition. This addition has no other effect on the properties of the composition than to prevent fermentation of the carbohydrates present in it.

It is also desirable, though by no means essential, to include in the composition a small proportion of a water-soluble salt of phosphoric acid, as for example trisodium phosphate or sodium hexametaphosphate (Calgon). The dosage may be of the order of 1% of the dry weight of the composition. The phosphates inhibit precipitation of insoluble calcium alginate when hard waters are used for dilution. They also, in some cases, improve the spreading qualities of the composition, particularly where its viscosity is high and it is considered undesirable to reduce the viscosity by further dilution.

It is impossible to fix any absolute limits to the dosage of any component of the composition, for the reason that some part of the benefit of each component will be realized from even the smallest dosage. But experience has indicated that the ranges of practical utility in the relation

of each component to the other are about as follows:

Concentration of algin in water vehicle——per cent—	From 2 to 10
Relation of algin to accelerator—	From 1:30 to 1:5
Relation of algin to humectant as—	
Sorbitol—	From 1:1 to 1:6
Glycerine—	From 1:04 to 1:2.4
Relation of accelerator to humectant—	From 1:1 to 30:1

In the making of oil-proof papers, two or more sheets of relatively thin paper are cemented together by interposed films of the composition, and may further be coated on one side or both sides of the assembly. The laminated paper thus produced has a very high tensile strength and when produced in suitable thicknesses is highly adapted to the making of cartons.

If the carton is additionally to be water-proofed on the outside, the oil-proof coating should be omitted from one side of the laminated sheet.

I claim as my invention:

1. A film-forming composition for use in the manufacture of oil-proof containers from paper, consisting substantially of: an algin selected from the group consisting of the alginates of the alkali metals, magnesium and ammonium; an adhesion accelerator selected from the group consisting of the sugars and the solubilized starches; a humectant selected from the group consisting of the polyhydric alcohols, and water as a vehicle, in which the weight relation of said algin to said adhesion accelerator is within the range from about 1:5 to about 1:30.

2. A film-forming composition for use in the manufacture of oil-proof containers from paper, consisting substantially of: an algin selected from the group consisting of the alginates of the alkali metals, magnesium and ammonium; an adhesion accelerator selected from the group consisting of the sugars and the solubilized starches; a humectant consisting of sorbitol, and water as a vehicle, in which the weight relation of said algin to said sorbitol is within the range from about 1:1 to about 1:6.

3. A film-forming composition for use in the manufacture of oil-proof containers from paper, consisting substantially of: an algin selected from the group consisting of the alginates of the alkali metals, magnesium and ammonium; an adhesion accelerator selected from the group consisting of the sugars and the solubilized starches; a humectant selected from the group consisting of the polyhydric alcohols, and water as a vehicle, in which the weight relation of said algin to said humectant is within the range from about 2.5:1 to about 1:2.5.

4. A film-forming composition for use in the manufacture of oil-proof containers from paper when dispersed in water as a vehicle, consisting substantially of: an algin selected from the group consisting of the alginates of the alkali metals, magnesium and ammonium; an adhesion accelerator selected from the group consisting of

the sugars and the solubilized starches, and a humectant selected from the group consisting of the polyhydric alcohols, in which the weight relation of said algin to said adhesion accelerator is within the range from about 1:5 to about 1:30.

5. A film-forming composition for use in the manufacture of oil-proof containers from paper when dispersed in water as a vehicle, consisting substantially of: an algin selected from the group consisting of the alginates of the alkali metals, magnesium and ammonium; an adhesion accelerator selected from the group consisting of the sugars and the solubilized starches, and a humectant consisting of sorbitol, in which the weight relation of said algin to said sorbitol is within the range from about 1:1 to about 1:6.

6. A film-forming composition for use in the manufacture of oil-proof containers from paper when dispersed in water as a vehicle, consisting substantially of: an algin selected from the group consisting of the alginates of the alkali metals, magnesium and ammonium; an adhesion accelerator selected from the group consisting of the sugars and the solubilized starches, and a humectant selected from the group consisting of the polyhydric alcohols, in which the weight relation of said algin to said humectant is within the range from about 2.5:1 to about 1:2.5.

7. A sealing composition adapted for attaching caps to cylindrical containers when brought to the consistency of a viscous liquid with water, consisting of about 4 parts of an algin selected from the group consisting of the alginates of the alkali metals, magesium and ammonium, about 20 parts of glucose and about 5 parts of sorbitol.

8. A sealing composition for attaching caps to cylindrical containers consisting of about 4 parts of an algin selected from the group consisting of the alginates of the alkali metals, magnesium and ammonium, about 20 parts of glucose and about 5 parts of sorbitol, with water sufficient to bring said components to the consistency of a viscous fluid.

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