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2,835,595

PACKAGING MATERIAL

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This invention relates generally to regenerated cellulose film and more particularly to a process for applying to such film a polymeric gas permeable coating and the resulting product.

Recently a moistureproof polymeric dispersion type coating has been found for cellophane which is superior to lacquer-coated cellophane sheets presently being used. The polymeric coating of this superior cellophane sheet not only is moistureproof, heat sealable, flexible and transparent, but also is a coating which tightly adheres to the base film even under high moisture conditions. While its moistureproof abilities are desirable for packaging fresh foods it has, however, been found that it is not readily adaptable for packaging fresh meat, fish, fruits and vegetables probably because of the fact that such polymeric dispersion coated cellophane, especially those of the vinylidene chloride type are not always gas permeable. And although it is known that plasticizers induce gas permeability it is not always an easy matter to use this knowledge to produce gas permeable films as all plasticizers are either not sufficiently useful or sufficiently operable with all polymers. Development of a moistureproof, gas-permeable polymeric coated cellophane, which would be superior to the lacquer coated cellophanes presently being used for fresh food wraps, therefore, has been retarded.

An object of this invention is the production of a packaging film, in particular, a regenerated cellulose sheet which not only is moistureproof, heat sealable, damage resistant and having a self-anchoring coating but also substantially gas permeable. A further object of this invention is the production of a sufficiently moistureproof, gas permeable, polymeric, dispersion type coated transparent film which is especially adapted for packaging fresh meat, fish, fruits and vegetables. Additional objects will become apparent to those skilled in the art upon a reading of the following detailed description.

In accordance with the objects enumerated above it has been found that a moistureproof gas permeable polymeric dispersion coated cellophane wrapping material will be produced if one incorporates certain specific plasticizers into a vinylidene chloride-methyl acrylate dispersion coating prior to the coating operation of the cellophane sheet. More specifically, it has been found that if one incorporates 2-ethyl hexyl diphenyl phosphate, tri-n-butyl aconitate, or butyl phthalyl butyl glycolate into a vinylidene chloride-methyl acrylate dispersion coating composition prior to coating a cellophane sheet there will be effected a coated cellophane sheet which is sufficiently gas permeable to make it especially adaptable for preserving fresh meat, fish, fruits and vegetables. This sheet will not only possess the desired moistureproofness which vinylidene chloride-methyl acrylate polymeric dispersion coatings render to cellophane but also will possess the desired gas-permeability for the specific wrapping requirements encountered.

This invention may be more aptly described by a ref-

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erence to an example which discloses a technique that may be used in formulating the coated film of this invention which is especially adapted for packaging fresh meat and although this technique specifically involves the packaging of fresh meat it is to be noted that other foods aforementioned could also be wrapped in similarly coated cellophane sheets if certain minor variations were made, such as in the degree of moistureproofness of the film.

A coating composition is made according to one of the procedures described in U. S. 2,570,478. One such procedure involves the following steps:

Four hundred parts of water, 2 parts of ammonium persulphate and 8 parts of Duponol ME (sodium lauryl sulfate) are placed in a vessel and stirred until a solution is formed. Three hundred eighty parts of vinylidene chloride, 20 parts of methyl acrylate, and 8 parts of itaconic acid are then mixed and added to this solution followed by one part of meta-sodium bisulfite as an initiator. The entire charge is then reacted while being stirred under reflux at a temperature of approximately 30°-60° C. At the end of the polymerization (indicated by the cessation of vinylidene chloride reflux), the mixture is stirred for an additional thirty minutes. Sixteen parts of a stabilizer such as Duponol ME (sodium lauryl sulfate) are then added to the dispersion after the reflux ceases. A stabilized dispersion is thereby formed.

To effect the objects of this invention, an external type plasticizer which is non-toxic and which is compatible with the polymers of the dispersion is then added thereto. The following technique may be used in such an addition:

The dispersion is first diluted with one-hundred parts of water. Then approximately one-hundred five parts of 2-ethyl hexyl diphenyl phosphate (resulting in approximately twenty parts of plasticizer per eighty parts solid content contained in the dispersion) is added slowly with vigorous agitation (total solids content of 50% or higher will thereby result). The agitation of the dispersion is continued for five to ten minutes after the completion of the addition and it is then aged for a period of 24-48 hours to permit complete diffusion of the plasticizer into the polymer particles. If desired, this aging period may be shortened by heating the mixture for a period of time; slip agents, hydrogen peroxide, stabilizer, coloring materials, additional plasticizers, etc., may then be added after the aging period if desired.

A transparent film, in particular, a glycerol softened regenerated cellulose base sheet, is then coated on one side with this dispersion with standard coating apparatus and procedures. The coated film may then either be rolled or placed in sheet form for ready subsequent use.

Fresh meat may then be wrapped with this coated cellulose film. The coated cellophane is used so that the uncoated side touches the enclosed meat while the moistureproof polymeric dispersion coated side faces the atmosphere. It is found that such wrapping will cause the packaged fresh meat, when stored under refrigerating conditions, to retain its appearance of freshness and "bloom" for an unexpectedly longer time than heretofore experienced.

In a similar manner the other plasticizers; namely, tri-n-butyl aconitate and butyl phthalyl butyl glycolate may also be incorporated into a similar coating composition prior to the latter's use for coating a cellophane base sheet. They should preferably be of a concentration of from 15-25% so as to produce optimum results.

It has been found that the base sheet should preferably contain a glycerol concentration of from 16-22% after it is coated for the most effective results. Concentrations greater or less than this range, while operable, will give inferior results as compared to the presently

known wrapping existing in the market. This may be due to the fact that cellophane becomes increasingly oxygen permeable as the film is softened with glycerol up to a peak value of 22% glycerol. A concentration above 22%, while having only a slight effect upon the oxygen permeability of the film, seems to adversely affect the moistureproof characteristics of the film. Where other softeners are used such as ethylene glycol, polyethylene glycol, etc., it may be necessary to determine other concentrations of softener required to give optimum oxygen permeability and moistureproof values.

It has also been found that to obtain optimum results, it is necessary to maintain the concentration of methyl acrylate in the polymer composition to a range of about 2% to about 12%. While concentrations other than these are operable they give inferior results because they produce inferior coatings.

So that this invention may be completely understood, an attempt is here made at explaining the reasons for the success attained by the wrapping packaging material of this invention. It is, however, to be specifically understood that this invention should not be limited by the correctness of the explanation which is here attempted.

Discoloration of packaged red meat is apparently due to an action of oxygen upon hemoglobin present in all fresh meat. When this hemoglobin is exposed to oxygen, it either picks up oxygen forming oxyhemoglobin or is actually oxidized to form methemoglobin depending upon the oxygen pressure surrounding the meat, the lower pressures favoring the methemoglobin. Oxyhemoglobin is responsible for the attractive bright red color, so characteristic of freshly cut meat while methemoglobin is dark brown in color and is representative of deteriorated meat.

Meat upon being cut and wrapped is believed to take up the excess oxygen contained in the package to form oxyhemoglobin, the attractive bright red colored substance. But such taking up of oxygen causes a reduction in the oxygen pressure. The hemoglobin not converted to oxyhemoglobin then is induced to form methemoglobin in view of the low pressure in the package. The meat then slowly acquires a dark brown color, this latter coloring forming more rapidly as the pressure decreases. This latter undesired reaction can be upset somewhat by using a film having high oxygen transmissibility. This will prevent to an extent the state of reduced oxygen pressure surrounding the meat and thereby prevent the formation of the undesired methemoglobin. The meat will, therefore, retain its attractive appearance for a longer period of time.

The coated plastic film of this invention has been found to possess not only the required gas-permeability but also additional advantages which are useful to the trade. Since only a one side coated plastic film is needed for wrapping the fresh foods discussed it eliminates the need for a double coating operation. Also, since it does not require a solvent for applying the coating as in a lacquer coated cellophane no solvent recovery step is required. Manufacturing costs are thereby reduced. There is also improved slip and improved heat-seal abilities and the film is found to be less susceptible to damage by extraneous forces. These all add to the attractiveness of the polymeric gas permeable coated film of this invention.

While a detailed description of this invention has been provided it is realized that those skilled in the art may make modifications in and adaptations of the process described above without departing from the spirit and scope of this invention. It is, therefore, to be specifically understood that such obvious modifications are to be considered within the scope and spirit of the herein described article and process.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is as follows:

1. A sheet especially adapted for packaging use, comprising a softened regenerated cellulose pellicle coated with a vinylidene chloride-methyl acrylate polymeric having a plasticizer selected from the group consisting of 2-ethyl hexyl diphenyl phosphate, tri-n-butyl aconitate and butyl phthalyl butyl glycolate incorporated therein.

2. A sheet especially adapted for packaging use, comprising a softened regenerated cellulose pellicle coated on one side with a vinylidene chloride-methyl acrylate polymeric having about 15-25% of a plasticizer selected from the group consisting of 2-ethyl hexyl diphenyl phosphate, tri-n-butyl aconitate and butyl phthalyl butyl glycolate incorporated therein.

3. The sheet of claim 1 in which the coated pellicle has a glycerol content as a softener in the range of 16-22%.

4. A sheet especially adapted for packaging use comprising a softened regenerated cellulose pellicle coated with a vinylidene chloride-methyl acrylate polymer having 2-ethyl hexyl diphenyl phosphate incorporated therein.

5. A sheet especially adapted for packaging use comprising a softened regenerated cellulose pellicle coated with a vinylidene chloride-methyl acrylate polymer having tri-n-butyl aconitate incorporated therein.

6. A sheet especially adapted for packaging use comprising a softened regenerated cellulose pellicle coated with a vinylidene chloride-methyl acrylate polymer having butyl phthalyl butyl glycolate incorporated therein.

7. The sheet of claim 4 in which the 2-ethyl hexyl-diphenyl phosphate comprises about 15-25% of the vinylidene chloride-methyl acrylate polymer coating.

8. The sheet of claim 5 in which the tri-n-butyl aconitate comprises about 15-25% of the vinylidene chloride-methyl acrylate polymer coating.

9. The sheet of claim 6 in which the butyl phthalyl butyl glycolate comprises about 15-25% of the vinylidene chloride-methyl acrylate polymer coating.

10. A package comprising meat wrapped in a softened regenerated cellulose pellicle coated on the outer side with a vinylidene chloride-methyl acrylate polymer having a plasticizer selected from the group consisting of 2-ethyl hexyl diphenyl phosphate, tri-n-butyl aconitate, and butyl phthalyl butyl glycolate incorporated therein.

11. A package comprising meat wrapped in a softened regenerated cellulose pellicle coated on the outer side with a vinylidene chloride-methyl acrylate polymer, said coating having about 15-25% of a plasticizer selected from the group consisting of 2-ethyl hexyl diphenyl phosphate, tri-n-butyl aconitate and butyl phthalyl butyl glycolate incorporated therein.

12. The method of packaging meat, fruits and vegetables in a preservative type of wrapper comprising packaging the food by wrapping it with a one side coated softened regenerated cellulose pellicle, the uncoated side to the food and said coating comprising a vinylidene chloride-methyl acrylate polymer having a plasticizer selected from the group consisting of 2-ethyl hexyl diphenyl phosphate, tri-n-butyl aconitate and butyl phthalyl butyl glycolate incorporated therein.

13. The process of producing a preservative type of cellophane wrapping comprising coating a cellophane base sheet with an aqueous dispersion of a vinylidene chloride-methyl acrylate polymer having a plasticizer selected from the group consisting of 2-ethyl hexyl diphenyl phosphate, tri-n-butyl aconitate and butyl phthalyl butyl glycolate incorporated therein and then drying.

14. The process of producing a preservative type of cellophane wrapping comprising coating a cellophane base sheet with an aqueous dispersion of a vinylidene chloride-methyl acrylate polymer having 15-25% of a plasticizer selected from the group consisting of 2-ethyl

hexyl diphenyl phosphate, tri-n-butyl aconitate and butyl phthalyl butyl glycolate incorporated therein and then drying.

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