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DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.

Letter Circular LC-455

Replaces LC-402

November 7, 1935.

TRANSPARENT WRAPPING MATERIALS

The widespread use of transparent wrapping materials in sheet form for packaging purposes has resulted in numerous inquiries regarding these materials. Frequently the substance of the inquiries has indicated that the nature of these products is not generally understood. By far the most frequently received inquiry, for example, has been that regarding solvents for regenerated sheet cellulose, which is not soluble in the ordinary sense in any solvent. Such an inquiry indicates that regenerated cellulose is confused with the cellulose esters, which is not surprising since in sheet form the two materials do not differ greatly in appearance. It is the purpose of this letter circular to give general information about the materials and to direct the reader to sources where detailed or special information may be obtained.

The materials described in this circular are those which represent continuous films and do not include paper treated to render it semi-transparent. Much of the information is acknowledged to be somewhat elementary in character, the effort being made to provide information for the individual not familiar with the technology of modern plastics. The references to the literature are selected and do not represent a complete bibliography. The materials mentioned in this circular are all patented. References to the patents may be found in "Chemical Abstracts" published by the American Chemical Society. This journal may be found in public libraries and the libraries of universities and technical schools.

REGENERATED SHEET CELLULOSE

Regenerated sheet cellulose is marketed under the tradenames of Cellophane and Sylphwrap.

Manufacture.

The raw material for cellophane is cellulose, the principal building material of the cell walls of plants. Its chief sources are wood and cotton. To better understand the reactions which occur during the manufacture of cellophane, cellulose, which has the empirical formula $C_6H_{10}O_5$, may be regarded as behaving in its reactions like an alcohol. Its formula will therefore be written as $C_6H_9O_4OH$ to indicate the presence of a hydroxyl (OH) group, which is characteristic of an alcohol.

In the manufacture of cellophane, wood pulp or cotton linters, the short-fibered cotton attached to the cotton seed, is first treated with an 18- to 20-percent water solution of sodium hydroxide (caustic soda, lye) for a definite period of time at a definite temperature. In this treatment the cellulose fibers swell, become translucent, and acquire a silky appearance. The change taking place involves the reaction between the alkali and the hydroxyl group of the cellulose which is expressed as:

$$C_6H_9O_4OH + NaOH = C_6H_9O_4ONa + H_2O$$

The resulting product is known as sodium cellulose. The reaction is analogous to that between ethyl alcohol and sodium hydroxide resulting in the formation of sodium ethylate:

$$C_2H_5OH + NaOH = C_2H_5ONa + H_2O$$

After a period of aging the sodium cellulose is treated in air-tight drums with carbon disulphide, which results in the formation of sodium cellulose xanthate. The formation of alkali xanthate is a general reaction. Thus the addition of carbon disulphide to sodium ethylate, whose formation is shown above, yields sodium ethyl xanthate:

$$C_2H_5ONa + CS_2 = C \begin{array}{l} \diagup O-C_2H_5 \\ = S \\ \diagdown SNa \end{array}$$

Likewise the reaction with sodium cellulose is:

$$C_6H_9O_4ONa + CS_2 = C \begin{array}{l} \diagup O-(C_6H_9O_4) \\ = S \\ \diagdown SNa \end{array}$$

The sodium cellulose xanthate is dissolved in a dilute solution of sodium hydroxide. The resulting solution is orange colored and of the consistency of corn syrup. It is known technically as viscose. It is very unstable and undergoes a series of reactions, which are not clearly understood, but involve the formation of a more complex molecule. The changes taking place affect the coagulability of the viscose. The change in this property is closely followed during a period of "ripening". After sufficient "ripening" the solution is ready for regeneration.

In the formation of the regenerated film of cellulose, the viscose solution is forced through a narrow slot and passes immediately into an acid solution which contains sulphuric acid and sodium sulphate. The regeneration takes place in two stages: first, the coagulation of the viscose by the sodium sulphate simultaneously with the neutralization of the alkali by the sulphuric acid; and second, the decomposition of the cellulose xanthate to hydrated cellulose through the continued action of the acid. The reaction between sodium cellulose xanthate and sulphuric acid results in the recovery of the cellulose, the liberation of carbon disulphide, and the formation of sodium acid sulphate. The reaction may be expressed as:

$$C \begin{cases} O-(C_6H_9O_4) \\ = S \\ SNa \end{cases} + H_2SO_4 = C_6H_9O_4OH + CS_2 + NaHsO_4$$

In the manufacture of regenerated cellulose in tubular form the viscose solution is extruded into the acid solution as a seamless tube supported by a mandrel.

After the precipitation of the hydrated cellulose film, it passes over rolls into water to remove acid and salts; through a solution which may contain sodium hydroxide or sodium sulphite to remove residual sulphur, and through a bleaching bath containing sodium hypochlorite, followed by further washing in water. Finally it is bathed in a solution of water and glycerol. The glycerol which remains in the dried film imparts pliability to the finished material. The process from the coagulation of the viscose to the finished film is continuous and progressive.

Chemical Properties

It is desirable to remember that fundamentally the chemical composition of cellophane is the same as that of the raw cellulose. The process of manufacture may be expressed as a cycle:

Cellulose (wood, cotton) ⟶ sodium cellulose

↓

sodium cellulose xanthate

↓

Cellulose (regenerated film) ⟵ viscose

Cellophane has all the chemical properties of cellulose. It swells in a sodium hydroxide solution. It undergoes all the typical cellulose reactions such as formation of the nitrate, acetate, ethyl ether, and xanthate. When ignited it burns with about the same flame as newsprint. It can not be dissolved in organic solvents such as alcohol, acetone, and esters. It differs in this respect from cellulose nitrate and acetate, which enter into the composition of lacquers and plastics.

Physical Properties

Cellophane is characterized by considerable tensile strength but very low resistance to tearing. The tensile strength is greatest in the direction of the movement of the film during its manufacture. The weight required to break a 1.62-inch strip having a thickness of 0.001 inch is stated to be about 15.7 lbs. in the longitudinal direction and 7.3 lbs. in the transverse direction.

Perhaps the most interesting of its properties is its permeability to gases, water vapor, and ultraviolet light. The material is practically impermeable to hydrogen and helium but readily allows the passage of oxygen, carbon dioxide, and water vapor. Toward water solutions it behaves as a dialyzing membrane, permitting the separation of substances of varying molecular size. It has been found particularly useful in this respect in the field of biological chemistry and the separation of substances whose acidities or alkalinities are not excessive.

The transparency of cellophane to light waves in the therapeutic region, 2900 A to 3100 A, is stated to be about 70 per cent. It has been suggested as a window material in the treatment of disease by heliotherapy since it does not lose a great deal of its transparency upon prolonged exposure to ultraviolet light.

Moisture-Proofed Cellophane

For a great many packaging purposes it is imperative that the passage of moisture through the film be prevented. To render the film moisture-resistant it is coated with a solution containing cellulose nitrate, which may also contain gums, resins, and plasticizers, in a lacquer solvent. Upon evaporation of the solvent the material is covered with a thin film which is less permeable to water vapor than the plain cellophane.

Adhesives

Fabrication of cellophane into articles requires the use of an adhesive. For plain cellophane, water-soluble adhesives such as mixtures of glue and glycerol are employed where a strong bond is desired. For use particularly on the moisture-proofed material a special adhesive containing cellulose nitrate is employed.

CELLULOSE ACETATE

Cellulose acetate sheet for wrapping purposes is sold under the trade names of Kodapak and Protectoid.

Manufacture

Cellulose acetate is a derivative of cellulose which belongs to a type of organic compound known as an ester. An ester is the product of the reaction between an acid and an alcohol. For example the reaction between acetic acid and ethyl alcohol yields the ester, ethyl acetate, and water. The reaction is represented as:

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

In the preparation of cellulose acetate the same reaction takes place. In this reaction cellulose is represented as a polyalcohol the three hydroxyl (OH) groups of which are replaced by acetate (CH_3COO) groups. The reaction may be represented as:

$$3\ CH_3COOH + C_6H_7O_2 \begin{cases} -OH \\ -OH \\ -OH \end{cases} = \begin{matrix} CH_3COO \\ CH_3COO \\ CH_3COO \end{matrix} \Big\rangle - C_6H_7O_2 + H_2O$$

Cellulose acetate is prepared by treating cellulose in the form of cotton fibers, linters, or paper, with a mixture of acetic acid and acetic anhydride. In practice the reaction is carried out in the presence of a small amount of sulphuric acid which acts as a catalyst, that is serves to assist the reaction. In order to obtain a material having the desired physical properties, including solubility in a wider range of solvents than the triacetate, the solution of the triacetate in acetic acid containing excess acetic anhydride is gradually diluted with water. This results in a mild hydrolysis or the removal of one or more acetate groups and replacement with hydroxyl groups. The reaction may be represented as:

$$\left.\begin{array}{l} CH_3COO \\ CH_3COO \\ CH_3COO \end{array}\right> C_6H_7O_2 + H_2O = \left.\begin{array}{l} OH \\ CH_3COO \\ CH_3COO \end{array}\right> C_6H_7O_2 + CH_3COOH$$

The diacetate pictured above does not represent the precise formula of the product obtained in practice. It is likely to be a mixture of hydroacetates. The solution of partially hydrolyzed cellulose acetate in 90 to 95 percent acetic acid is then poured into an excess of water which precipitates the flocculent cellulose hydroacetate, which is washed and dried.

The resulting product is suitable for a variety of purposes including the manufacture of molded plastics and film. Cellulose acetate is produced in sheet form about 0.001 inch in thickness for wrapping purposes. The method of manufacture is that known as the casting process. The cellulose acetate is dissolved in a suitable volatile solvent and a liquid having a very low vapor pressure, or a minimum tendency to evaporate, known technically as a plasticizer is added. This solution is then permitted to flow in a carefully regulated stream onto the highly polished surface of a large metal drum. The drum is revolved in a chamber in which the atmospheric conditions are regulated and a means is provided for the constant removal and recovery of the evaporating solvent. The dried film deposited upon the drum is then removed in the form of a continuous sheet.

Properties

Cellulose acetate differs from cellulose in being thermoplastic, that is capable of being softened by heat, and in being soluble in numerous organic solvents such as acetone, diacetone alcohol, methyl acetate, methyl cellosolve, chloroform, and two-type solvents such as a mixture of ethylene chloride and ethyl alcohol. Cellulose acetate is more water-resistant than regenerated cellulose. The material has a comparatively high ignition temperature and burns slowly. It is also resistant to the embrittling effects of exposure, particularly to sunlight. In these latter two properties it differs materially from cellulose nitrate, erroneously called nitrocellulose. To render cellulose acetate flexible it is the practice to include a plasticizer in its composition. Such substances are liquids having very low vapor pressures, or a minimum tendency to evaporate. Among the substances employed may be mentioned triacetin, diethyl phthalate, and dibutyl tartrate. These are by no means all. Numerous other plasticizers are mentioned in the patent literature.

The chief property which recommends the use of cellulose acetate for wrapping purposes is its ability to withstand changes in atmospheric humidity without change in physical properties. This is due to its own low hygroscopicity and the absence of a moisture-absorbing plasticizer such as glycerol. Its solubility in organic solvents and its thermoplasticity make the sealing of the material and the formation of seams a comparatively simple matter.

RUBBER HYDROCHLORIDE

By treatment of unvulcanized rubber with hydrochloric acid a product is obtained which is known as rubber hydrochloride. The reaction undoubtedly involves, in addition to the combining of rubber with hydrochloric acid, a change in the nature of the rubber molecule and the product cannot be definitely expressed. The material differs from the parent rubber in its properties, particularly in the reduction of the plastic extensibility of the latter. The extent of the change depends upon the extent of the treatment accorded the rubber.

A material of this nature is manufactured in thin sheets and marketed under the trade name Pliofilm. Details of manufacture do not appear in the literature. The material is colorless and transparent and bears a close resemblance to regenerated cellulose and cellulose acetate sheet in appearance and "feel". The claims of the manufacturer are:

"The tensile strength is only approximately one-half that of regenerated cellulose sheet but the tear resistance is more than twice that of the latter. It is waterproof and not affected by changes in humidity and is resistant to the action of oils and greases. It has a lower specific gravity than cellulose. It may be heat-sealed although the range of heat-sealing must be carefully controlled within a temperature range of 105 to 130° C."

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