

## UNITED STATES PATENT OFFICE

2,542,052

POLYVALENT METAL PECTINATE FILMS  
AND PROCESS OF PRODUCING SAME

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to us of any royalty thereon.

This invention relates to films, and in particular to films which are essentially composed of a polyvalent metal salt of a pectinic acid having a methoxyl content not greater than 7.4%. The pectinic acid utilized is of high molecular weight with consequent high viscosity of water solutions or dispersions thereof. It may be produced by partial demethoxylation of pectin (pectin being the usual preparation of commerce extracted from various plant products, such as citrus peel or apple pomace without substantial demethoxylation) according to known procedures (see Patent No. 2,358,430, for example).

The "pectinic acid" herein referred to should be distinguished from "pectic acid," the latter term pertaining to the acid produced by substantially complete demethoxylation of pectin. Pectinic acid has a methoxyl content between that of pectin and pectic acid, pectin having a methoxyl content of about 10 to 14 percent depending largely on the source thereof. The methoxyl content of the pectinic acid may vary over a considerable range depending on the process of demethoxylation employed.

Superior films, from the standpoint of forming water-resistant films, are made from pectinic acids having a methoxyl content of below 6 percent. Films having greater elasticity can be made from pectinic acids having a higher methoxyl content. In general, according to the invention, the film is formed essentially from a polyvalent metal salt of a pectinic acid having a methoxyl content not greater than 7.4%. The salt above referred to means a salt of a pectinic acid with a polyvalent metal and is intended to include acid salts, i. e., those in which the carboxyl groups are not completely salified with the polyvalent metal.

According to one process of preparing the films, an aqueous solution of pectinic acid is first neutralized or partially neutralized with an inorganic hydroxide, such as an alkali metal or ammonium hydroxide, thus to form an alkali metal salt of the acid, an alkali metal hydrogen salt of the acid, an ammonium salt or an ammonium hydrogen salt of the acid. This material is then formed into an initial film and this film is immersed in an aqueous solution of a polyvalent metal salt.

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The initial film can be formed in any desired manner, for instance, by extrusion into an alcohol solution, dipping, or simply by allowing a solution of the pectinate material to dry on a flat surface. Any suitable polyvalent metal salt can be used for making the solution in which to dip the initial film, for instance, calcium chloride, chromium chloride, aluminum chloride, aluminum sulphate, zinc chloride, zinc sulphate, zinc nitrate, barium chloride, magnesium sulphate, magnesium chloride, strontium chloride, and suitable salts of titanium, molybdenum, iron, nickel, cobalt, copper, mercury, cadmium, lead and tin. It is only necessary that the solution contain the cations corresponding to the desired metal. Mixtures of salts, such as a mixture of calcium chloride and zinc chloride, can be used to obtain a film containing mixed metals, such as zinc and calcium. Concentration of the salt is not critical, and generally solutions of one normal concentration give good results. The metathesis takes place quite rapidly; generally 1 to 30 minutes yields complete reaction.

Examples I to XI exhibit the invention in detail according to the process more generally set forth above. In these examples, the intrinsic viscosity data were obtained in the usual manner expressing the concentration as grams of pectinic acid per 100 ml. of solution. The measured solutions contained 0.9 percent sodium chloride in order to suppress the electro-viscous effect. The intrinsic viscosity was given by the expression:

$$\text{Limit}_{c \rightarrow 0} \left( \frac{\eta_{sp}}{c} \right)$$

where

c is concentration

$\eta_{sp}$  is specific viscosity

## EXAMPLE I

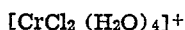
A sample of pectinic acid having an intrinsic viscosity of 5.2 and a methoxyl content of 4.5 percent was stirred with sufficient water to give a 1 percent solution, and sufficient 0.5 N sodium hydroxide was added slowly with rapid stirring to raise the pH of the solution to 4.0. The solution was stirred for at least 30 minutes then centrifuged to remove suspended matter. Since the pectinic acid was approximately half-neutralized at the pH 4.0 indicated, the resulting material was a solution of sodium hydrogen salt of the pectinic acid.

Portions of the clarified solution were pipetted into shallow trays and evaporated. The result-

ing transparent, colorless films were carefully stripped from the trays.

A strip of the thus prepared sodium hydrogen salt of the acid film was gently stirred in a 1.0 N aqueous solution of calcium chloride at 25° C. for 5 minutes. The strip of polyvalent metal salt of the pectinic acid thus formed was thus washed with distilled water and dried by inserting between 2 pieces of filter paper, covering with a piece of glass and a weight and allowing it to remain in this condition overnight.

In a number of other examples, the same general procedure was followed. In some of them, 30 parts of a plasticizer per 100 parts of pectinic acid were added to the solution of sodium hydrogen salt of the pectinic acid before it was centrifuged. Glycerol is a desirable plasticizer. When this plasticizer is used, the strips of a polyvalent metal salt of the acid should be washed in water containing glycerol, since if washed in water alone the glycerol tends to be washed from the films. Glycol bori-borate was also used as a plasticizer. Preparation of this plasticizer is disclosed in U. S. Patent 1,953,741. Also, in the other examples, the polyvalent metal cation was varied by using the chloride of the desired metal in place of the calcium chloride. When chromic chloride was used, the 1 N solution was heated to 55° to 60° C. for two hours and then allowed to stand overnight to convert the green form



to the violet form



Tests of the various films were made according to the procedure indicated, the various columns in Table 1 indicating the results under the appropriate headings.

The "Tensile strength at break" column is that of the dry films which were previously stored in a desiccator containing 36 percent sulfuric acid to provide a relative humidity of 65 per cent at 25° C. The wet tensile strength on which the "Wet strength" column is based was determined by soaking the film in distilled water for an hour and spraying with water while the films were in the testing machine. The last three columns indicate results of washing tests, the data showing the loss in weight with the strips washed, first, in distilled water at 25° C. for four hours; second, in 0.1 percent  $\text{Na}_2\text{CO}_3$  at 40° to 50° C. for one-half hour; and third, in 1 percent soap flakes at 40° to 50° C. for one-half hour; following the washing, the strips being rinsed in distilled water and dried at 65 percent relative humidity before final weighing.

Table 1

| Example   | Cation  | Plasticizer             | Tensile strength at break, lbs. per sq. in. | Elongation at break, per cent | Wet strength, per cent of dry | Loss of weight washed in water, per cent | Loss of weight washed in $\text{Na}_2\text{CO}_3$ , per cent | Loss of weight washed in soap, per cent |
|-----------|---------|-------------------------|---------------------------------------------|-------------------------------|-------------------------------|------------------------------------------|--------------------------------------------------------------|-----------------------------------------|
| I.....    | Ca..... | None.....               | 15,600                                      | 4.0                           | 21                            | 0                                        | 8                                                            | 5                                       |
| II.....   | Zn..... | do.....                 | 15,300                                      | 3.5                           | 28                            | 0                                        | 8                                                            | 9                                       |
| III.....  | Al..... | do.....                 | 15,400                                      | 3.0                           | 29                            | 0                                        | 100                                                          | 40                                      |
| IV.....   | Cr..... | do.....                 |                                             |                               |                               | 2                                        | 0                                                            | 0                                       |
| V.....    | Ca..... | Glycol bori-borate..... | 20,400                                      | 5.5                           | 20                            | 1                                        | 11                                                           | 8                                       |
| VI.....   | Zn..... | do.....                 | 21,000                                      | 6.5                           | 20                            | 1                                        | 3                                                            | 16                                      |
| VII.....  | Al..... | do.....                 | 17,700                                      | 3.5                           | 23                            | 0                                        | 100                                                          | 45                                      |
| VIII..... | Cr..... | do.....                 | 16,100                                      | 5.2                           | 28                            | 1                                        | 0                                                            | 0                                       |
| IX.....   | Ca..... | Glycerol.....           | 14,900                                      | 8.0                           | 28                            | 10                                       | 18                                                           | 20                                      |
| X.....    | Al..... | do.....                 | 13,900                                      | 4.7                           | 31                            | 10                                       | 100                                                          | 53                                      |

#### EXAMPLE XI

Calcium and zinc salts of pectinic acid films were prepared as set forth in Example I, but starting with a pectinic acid having an intrinsic viscosity of 4.4 and a methoxyl content of 7.4 percent. No plasticizer was used.

These films were tested in the same manner as set forth in the prior examples, the results being given in the following Table 2:

Table 2

| Test                                                             | Ca salt | Zn salt |
|------------------------------------------------------------------|---------|---------|
| 15 Tensile strength at break, lbs./sq. in.....                   | 14,600  | 14,400  |
| Elongation at break, percent.....                                | 6.5     | 8.0     |
| Wet strength, percent of dry.....                                | 10.0    | 17.0    |
| Loss of weight washed in water, percent.....                     | 1.5     | 0.5     |
| Loss of weight washed in $\text{Na}_2\text{CO}_3$ , percent..... | 23.0    | ~80     |
| Loss of weight washed in soap, percent.....                      | ~80     | 46.0    |

Another process of preparing the films involves extrusion through a die of a solution of pectinic acid, partly or completely neutralized with an alkali metal or ammonium hydroxide, into a solution of the polyvalent metal salt. In this process the initial aqueous solution may have a concentration of 1 to 5 percent and a pH of about 4 to 6. Stronger films are obtained at higher concentrations of pectinate, the limit of concentration being the ability to obtain a solution which is not too viscous to flow through the die. Any of the previously mentioned soluble polyvalent metal salts can be used in the polyvalent metal salt solution. Generally, aqueous solutions of these salts are satisfactory. In some cases, however, with the pectinic acids of higher methoxyl content, better results are obtained by including in the solution a substantial portion of an organic solvent such as ethyl alcohol.

Example XII exhibits the invention more specifically employing the above described procedure.

#### EXAMPLE XII

A pectinic acid having a methoxyl content of 3.5 percent and an intrinsic viscosity of 2.4 was stirred with water to give a 5 percent solution which was then treated with sodium hydroxide to give a pH of 5.0. This solution was extruded through a nozzle having a rectangular aperture of 0.7 mm. by 70 mm. into a precipitation bath consisting of 1 N calcium chloride and 0.02 N hydrochloric acid. The extrusion rate was approximately 2.6 ml. per second, and the film was drawn through the bath at the rate of 5.6 cm. per second. The bath had an effective length of 30 inches. The film was removed from the bath on godet rolls and passed into a water bath sufficiently long to give complete washing. After

drying, a strong film of the calcium salt of pectinic acid was obtained.

As before indicated, the films may contain water-soluble plasticizers. The plasticizer may be added to the solution from which the film is made. In the washing of films containing glycerol or other low molecular weight, water-soluble substances, the wash water should contain the same plasticizer to prevent removal of the plasticizer from the film by the wash water.

The incorporation of a plasticizer is advantageous to increase the stretch and improve the folding endurance of the film. Water-soluble plasticizers have proved best for this purpose, for instance, tartaric acid, glycol, glycol mono-methyl ether, glycol mono-ethyl ether, and so forth, in addition to those previously mentioned. The proportion of plasticizer should not be more than about 30 percent (based on the amount of pectinic acid). Higher proportions than this value tend to cause considerable reduction in the tensile strength of the film.

The films of this invention are self-sustaining, odorless, non-fibrous, transparent, flexible, and strong. They can be used for wrapping articles to protect them from dust, dirt, oil, or other contamination. The films of zinc, aluminum, and calcium pectinates, especially the first two mentioned, are particularly desirable, in that they are flame-resistant. Especially good flame-proofing films can be made by incorporating known flame-resisting agents, such as sodium boro-phosphate, for instance, into the zinc or aluminum salt of the pectinic acid film. The film of the calcium salt of the acid is non-allergenic and can be employed in surgical operations as a separatant to prevent adhesions. Copper, lead, zinc, and other salts of the acid form films which are toxic to micro-organisms and can be used to protect articles from such attack. Thus, a film of the zinc salt of pectinic acid can be employed to make cloth resistant both to flame and mildew.

Films produced according to the examples may be used as wrappings in the regular manner. However, they may also be used as permanent coatings by attaching them to articles with adhesives. A dispersion of the metal salt of the pectinic acid may be used as an adhesive for this purpose.

When it is desired that the film be permanently attached to the article, it may also be formed directly thereon by dipping the article in a hot dispersion of the polyvalent metal salt. Aqueous dispersions containing 1 to 8 percent of the polyvalent metal salt and heated to about 50° to 90° C. give best results. Upon immersion of the article in such dispersion, removal therefrom and exposure to air, a gel-like coating is formed. Upon drying, a tough film results.

If desired, a film may be formed on an article having a non-coherent surface, by dipping in the manner indicated above, and after drying, the film may be peeled from the article, thus to produce a separate film.

In order to obtain a dispersion of an efficient concentration, it is sometimes necessary in this type of procedure to limit the amount of polyvalent metal cation with respect to the carboxyl groups present in the pectinic acid. Generally, the proportion of polyvalent metal cation carboxyl groups ranges from completely salified to  $\frac{1}{2}$  salified. It has been found that if the pectinic acid has a low methoxyl content, it should be only partly salified. If on the other hand

the pectinic acid has a high methoxyl content, the carboxyl groups may in some case be substantially completely salified. The criterion here is to get a dispersion which is not too viscous to flow properly and one which will give a good gel-like coating when the article is immersed therein. Where the pectinic acid has been only partially salified, the film so formed can, if desired, be subsequently immersed in a solution containing the desired cation whereby all the carboxyl groups will become salified.

Having thus described the invention, what is claimed is:

1. A process of producing a film comprising pectinic acid having a methoxyl content not greater than 7.4% with an inorganic hydroxide at least partially to neutralize the pectinic acid, forming a film of the material thus obtained, and contacting the film with an aqueous solution of a water-soluble polyvalent metal salt.

2. The process of claim 1 characterized in that a water-soluble plasticizer in amount not to exceed 30 percent of the pectinic acid is mixed with the material before it is formed into the film.

3. The process of claim 1 characterized in that the film of the material is formed by plating the material onto a non-adherent surface and then peeling it from the surface, and thereafter contacting the film with the aqueous solution of the water-soluble polyvalent metal salt.

4. The process of claim 1 characterized in that the film of the material is formed and contacted with the aqueous solution of the water-soluble polyvalent metal salt by extruding the film of the material into the solution.

5. The process of claim 1 characterized in that the metal salt is one which yields zinc cations in the aqueous solution.

6. The process of claim 1 characterized in that the metal salt is one which yields calcium cations in the aqueous solution.

7. The process of claim 1 characterized in that the metal salt is one which yields chromium cations in the aqueous solution.

8. A film composed essentially of a polyvalent metal salt of a pectinic acid having a methoxyl content not greater than 7.4%.

9. A film composed essentially of a polyvalent metal salt of a pectinic acid having a methoxyl content not greater than 7.4% plasticized with a water-soluble plasticizer.

10. The film of claim 9 characterized in that the plasticizer is glycerol.

11. A film composed essentially of the zinc salt of a pectinic acid having a methoxyl content not greater than 7.4%.

12. A film composed essentially of the calcium salt of a pectinic acid having a methoxyl content not greater than 7.4%.

13. A film composed essentially of the chromium salt of a pectinic acid having a methoxyl content not greater than 7.4%.

14. The film of claim 11 plasticized with glycol bori-borate.

15. The film of claim 12 plasticized with glycol bori-borate.

16. The film of claim 12 plasticized with glycerol.

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