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FILM PRODUCTS HAVING PECTIN LAYERS

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Fig. 1

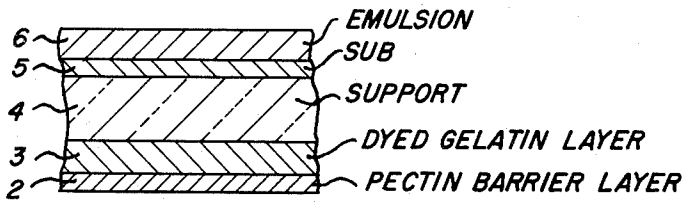


Fig. 2

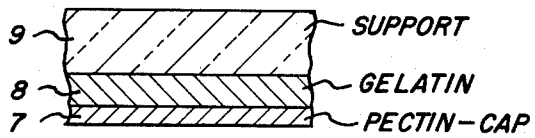
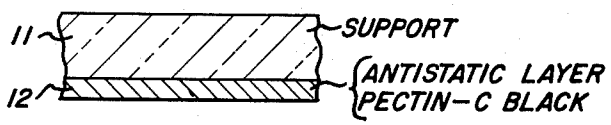


Fig. 3



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FILM PRODUCTS HAVING PECTIN LAYERS

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This invention relates to film products which carry a layer having a pectin content. More particularly, this invention concerns photographic film products which contain in their make-up as an essential component a layer containing pectin, especially low methoxyl pectin.

In the manufacture of photographic film products there is applied to a sheet material such as a film support or base various types of layers. For example, layers are applied for antistatic or antihalation purposes. Or layers may be applied for barrier purposes such as to prevent a dye or the like coloring material from migrating from one layer to another. There are also other types of layers. In connection with certain of the layers of the type described it may be desired that such layers remain on the film product through certain steps of processing but such layers are ultimately removable as respects the finished product.

Prior art products and procedures of the type indicated have possessed some disadvantages. In certain instances the materials employed for the various types of layers have comprised rather complex mixtures of material. In some instances the prior art type of coatings have either required high concentrations of materials which slowed down coating procedures or if lower concentrations were used for more rapid coating considerable time or special drying space and techniques were required for obtaining satisfactory results.

It is, therefore, apparent that the development of simpler and improved coatings for film products as well as procedures whereby the coatings may be applied in a more rapid manner represents a highly desirable result. After extended investigation we have discovered ways whereby improved coatings and procedures of the class indicated may be accomplished.

This invention has for one object to provide photographic film products which have in their make-up improved coatings carried by the film base. A particular object of this invention is to provide a photographic film product which is comprised of a film support that carries thereon a layer which contains a content of pectin. Another object is to provide film products of the class indicated which carry certain functional layers, which layers may be removed at the completion of processing steps. Still another object is to provide improved procedure whereby certain types of layers or coatings applied to photographic film products may be caused to set or gel at relatively faster speeds, even though the coatings have low concentration of solids. Still another object is to provide film products containing a variety of types of improved coatings such as barrier coatings, antistatic

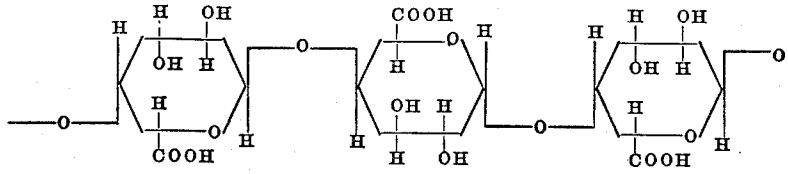
coatings, and the like. Other objects will appear hereinafter.

In the broader aspects of our invention we have found that the relatively readily available commercial material known as pectin (of a certain quality and composition as will be discussed in detail hereinafter) may be employed in various ways for improving the make-up and application of layers in photographic film products. The use of such pectin material not only is relatively simple but gives improved results as will be pointed out hereinafter. In further detail, we have found that pectin alone, or in mixture with small amounts of certain other components, the pectin still being the essential component, can be employed to produce barrier layers, antistatic layers and the like in photographic film products. While as just mentioned, pectin alone, or as the essential component, is preferred for producing such type of layers, certain amounts of other materials may be present in the layers for special effects as will be discussed in detail hereinafter.

Such pectin-containing layers in accordance with the present invention are not only simpler and less complex than prior art type of layers heretofore used but the layers are readily removable at the completion of photographic processing steps if it is desired to remove the layers from the finished photographic product.

In the preferred embodiment of this invention we have found that pectin designated as low methoxyl pectin should be used as this type of pectin when incorporated in gelatin solutions of low concentration will cause such solutions to more rapidly chill set. This is advantageous in not only permitting the utilization of lower concentration for coating purposes but permits more rapid coating procedures.

Pectin generally is a known material which may be obtained commercially. Hence, extensive general discussion of this material appears to be unnecessary. However, it appears desirable to point out that pectin contains pectic acid of the illustrated structure.



For general use we prefer to use pectin NF which contains more than 7% of methoxyl groups and not less than 78% of the pectic acid constituent.

For the gel setting species of the present invention we have found that there should be used low methoxyl pectin wherein the methoxyl content is between about 3 and 7%. Such low methoxyl pectins are a group of pectinic acids containing 2.5–7% methoxyl. They are commercially available. These low methoxyl pectins are usually prepared from the high ester pectins by partial deesterification accomplished by the use of acid, alkali or enzymes. Deesterification by means of concentrated ammonium hydroxide in water is accompanied by the formation in the pectinic acids of both —$CONH_2$ and —$COONH_4$ groups so that the resultant low methoxyl pectin will contain these in addition to the free carboxyl and methyl ester groups. It is known that low methoxyl pectins as just described will form gels in the presence of small amounts of poyvalent ions. We have further found that low methoxyl pectins will accomplish the result of improving the chill setting of gelatin solutions of relatively low concentration, the use of such low concentrations not heretofore being considered practical.

For a further understanding of our invention, reference will be made to the attached drawing forming a part of

the instant application, in which drawing a few of the embodiments of film products are shown. All of the figures on the drawing are cross sections on large scale of illustrated film products in accordance with the present invention.

Fig. 1 shows pectin-containing barrier layer **2** positioned over a dyed gelatin layer **3**. These layers are carried by film support **4**. The support also carries a sub layer **5** and an emulsion layer **6**. This pectin barrier layer will prevent the migration of dyes from the gelatin layer onto the emulsion layer when the film product is rolled up.

Fig. 2 shows a pectin-containing layer **7** which is positioned over gelatin layer **8**. These layers are carried on film support **9**. In this instance the pectin layer contains a matting agent—cellulose acetate phthalate (CAP)—which prevents ferrotyping of the emulsion layer when it is rolled up.

Fig. 3 shows a film or sheet **11** which would normally develop a static charge in handling. Applied thereto at **12** is a pectin antistatic layer which minimizes the static charge build-up.

For a further understanding of our invention, reference will now be made to the following examples which are set forth for illustrating certain embodiments.

Example I

This example is set forth for illustrating use of a pectin-containing layer of the present invention as a barrier layer for preventing dye offsetting. A 2% pectin solution (using pectin NF) was made up in distilled water. This was coated over a dyed gelatin pelloid carried on a film support as shown in Fig. 1. The coating was at the rate of 100 mg. of pectin per square foot of the coated surface in order to obtain a barrier layer as shown in Fig. 1. Upon tightly coiling the film product the dyes show no diffusion, not even into the pectin barrier layer. For further improving the pectin layer for barrier purposes, small amounts of mordants such as diphenyl or triphenylguanidine may be incorporated with the pectin. Such materials in combination with the pectin still further reduces any tendency of dyes to diffuse through the barrier layer since they are mordanted at the gelatin-pectin interface or only a short distance into the pectin layer.

Example II

This example is set forth for illustrating the use of pectin layers in accordance with the present invention for preventing ferrotyping. A 2% pectin solution as just described, was made up. Alkali soluble cellulose acetate phthalate was dispersed into this pectin solution by means of ball milling. This pectin-cellulose acetate phthalate coating was then applied over a gelatin layer as illustrated in Fig. 2. Any tendency toward ferrotyping when the film product was rolled upon itself or positioned in close contact with similar surfaces was eliminated.

Example III

This example is set forth for illustrating the use of pectin solutions (which pectin is free of buffer salts or sugars as above discussed) for antistatic purposes. 2% pectin solution was made up. This solution was coated by a conventional applicator roll coater onto various film products. That is, it was coated in a very thin layer onto cellulose acetate Cine film. It was also coated over film support which carried a gelatin layer. Also, certain of the 2% pectin solution was modified with the addition of Tamol P (the sodium salt of the condensation product of naphthalene sulfonic acid and formaldehyde) to the amount of 50–100 mg. per square foot. This addition to the pectin layer further decreased the surface resistivity. Into another amount of pectin solution there was incorporated a small amount of carbon black. This also produced a reduction in surface resistivity.

The various film products carrying a pectin layer made up in accordance with this example were tested and compared with an uncoated Cine cellulose acetate film. The results of these tests are set forth below.

	Surface resistivity, ohms
Safety Cine positive cellulose acetate support	$10{,}000\times10^{10}$
Pectin on SCP support	8×10^{10}
Dyed gelatin pelloid	12×10^{10}
Pectin over a dyed gelatin pelloid	0.77×10^{10}
Tamol P (the sodium salt of the condensation product of naphthalene sulfonic acid and formaldehyde) in pectin over a dyed gelatin pelloid	0.59×10^{10}
Gelatin pelloid	84×10^{10}
Pectin over gelatin pelloid	2.9×10^{10}
Cellulose ester-carbon black layer (no pectin)	0.32×10^{10}
Carbon black in pectin over gelatin layer	1.8×10^{4}

Example IV

As antihalation layer a dispersion of blue silver in gelatin was added to a 2% pectin solution as already described. This was then coated on safety Cine positive support as well as over a gelatin pelloid. The blue silver is partially removed in the initial washing and completely removed during processing. Bleachable oxonol dyes can be dispersed in 2% pectin solution and are removed in developer. Pigments, such as Prussian Blue or blue silver do not transfer or offset onto emulsions.

Example V

As a water insoluble barrier layer, low-ester pectins are readily dissolved in water which are free of polyvalent salts. A sample was coated over a gelatin layer which contained calcium acetate. The pectin solution set immediately and when dried was not removed by water. The layer was readily removed when sequestering agents such as Calgon (a sodium phosphate chemical commonly called "sodium hexametaphosphate"), Quadrafos (sodium tetraphosphate) or ethylenediaminetetraacetic acid were present.

Examples will now be set forth for illustrating the preferred species of the present invention relating to the use of low methoxyl pectin for improving the chill setting of low concentrations of gelatin. Heretofore the chill setting of low concentrations of gelatin (1.54–2.54%) by normal procedures has been avoided because such low concentration materials create certain problems. That is, air velocities must be decreased. Lower drying temperatures were required or the remelting of the gelatin occurred. Flat drying appeared to be the only feasible procedure.

In accordance with the present invention we have found that the addition of low methoxyl pectin to low concentration of gelatins so aids in the chill setting of the gelatin that normal air velocities and relatively high drying temperatures are possible. Up to about 10% pectin LM, based on the dry weight of the gelatin appears to be sufficient to accomplish this new result.

Example VI

To a 2½% clear gelatin solution was added 2½% solution of pectin LM. The ratios of gelatin to pectin were varied. Carbon black dispersion was added as an indicator. Sequestrene was added to chelate and suppress the action of residual calcium or other polyvalent ions on pectin. Saponin solution was added as a coating aid. The solutions were coated onto safety Cine support at the rate of 2 lbs. of solution per 100 sq. ft.

A jet of air equivalent to 5.7 inches water pressure/square inch was directed across the material as it came from the chill box at 40° F. Along the edge of the film a pressure streak was formed by holding the finger against the coated material. The air jet would indicate the gel

strength. The pressure streak was added to indicate any remelting of the gelatin-pectin mixture during drying.

Coating No.	Gel Solution	Pectin LM	Percent Gel	Percent Pectin
29	250	0.0	2.57	0
28	237.5	12.5	2.44	.13
27	225	25	2.30	.26
26	200	50	2.06	.52
25	175	75	1.80	.78
24	150	100	1.54	1.04

As determined from an inspection of the several coatings, the pressure streak on No. 29 has flowed back during drying whereas others have not.

Example VII

To 150 cc. 5% clear gelatin dispersion was added variable amounts of a 2½% solution of pectin LM. Carbon black was added as a density indicator. Sequestrene (ethylene tetraacetic acid) was added to chelate and suppress the action of calcium salts on pectin. Saponin was added as a coating aid. The solutions were diluted to 300 cc. to give a 2½% gelatin solution. The solutions were coated onto safety Cine support at the rate of 2 lbs. of solution per 100 sq. ft.

A jet of air equivalent to 6.2 inches water pressure/square inch was directed against the material (height 0.75 inch) as it came from the chill box. A pressure streak was also formed against the edge of the film.

Coating No.	5% Gel Solution	Pectin LM	Total Volume
32	150	12.5	300
31	150	25	300
30	150	50	300

As indicated on the film, coating No. 32 shows a streak created by the air jet, and the pressure streak along the edge has flowed together during drying. Nos. 30 and 31 show no air jet streak and the pressure streaks have not closed during drying. The coatings indicate that one part pectin LM in 11 parts gelatin is sufficient to set a 2½% gel solution so that it can be coated under normal coating conditions.

Viscosity Measurements at 140° F.	50 cc. Volumetric Pipette, seconds
2½% gel solution	12.0
7.5 g. gel+.38 g. pectin LM per 300 cc. DW	13.5
7.5 g. gel+.75 g. pectin LM per 300 cc. DW	16.0
7.5 g. gel+1.5 g. pectin LM per 300 cc. DW	25.8
7.5 g. gel+3.0 g. pectin LM per 300 cc. DW	31.0

In the above examples the measurement of surface resistivity of film may be accomplished in any suitable manner. The measure of resistivity of the surface is a convenient way for ascertaining the effectiveness of layers for antistatic purposes. Values below 1×10^{10} ohms indicate that the antistatic properties of the film thus treated will be quite satisfactory. Surface resistivity is resistance, measured in ohms, when a voltage is applied between two electrodes at a specified distance apart. It is measured in ohms per square (either centimeters or inches). This value may be measured by surface electrical resistance measuring apparatus. Such apparatus may be built around a Megometer type unit manufactured by the Freed Transformer Company, New York. The apparatus comprises two parallel electrodes on the film at fixed relative humidity conditions. These electrodes are long compared to the distance between them so as to avoid end effects. The observed resistance reading is divided by the distance between the electrodes and multiplied by the length to obtain the surface resistivity. A high voltage direct current charge is fed into the apparatus. A coating which reduces the surface resistivity below 1×10^{10} ohms indicates that it would provide good antistatic protection.

The particular apparatus used in measuring resistivity, however, is not a limitation on the present invention.

In the above table by DW we mean distilled water.

The 50 cc. volumetric pipette used for viscosity measurements is operated as follows:

A volumetric pipette, which has been previously calibrated against solutions of known viscosity, is filled to the upper mark with the solution to be measured. Time is measured from the moment the solution begins to flow from the upper mark until it reaches the lowest mark. The time required is a measure of the viscosity.

In the above examples where we have shown incorporating in the pectin layer various amounts of other materials such as carbon, CAP, and the like, the amount of such additions may be within the range of 10% to 80%. Also, in the above examples while we have described the use of 2% solutions and have found such concentrations to be quite satisfactory, our invention is not restricted thereto. Likewise, with respect to chill setting wherein we have described the use of 10% of pectin LM, with respect to the gelatin other amounts from 10% to 75% may be used. Although we have described our coatings as applied to safety film support which is of a cellulose acetate composition of above 38% acetyl, and usually within the range of 42–44.5% acetyl, our coatings may be applied to other film supports exemplified by polyester and polystyrene.

The use of saponin as a coating aid has been referred to inasmuch as this is a coating aid commonly used in the photographic industry. However, other coating aids known in the photographic art may be used.

In the above examples we have utilized the pectin either as an aqueous solution or by incorporating it into an aqueous solution of gelatin since the pectin is readily soluble in water.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. In a method of coating a gelatin solution having a low concentration of gelatin onto a film support the improvement feature which comprises incorporating into the low concentration gelatin solution a content of low methoxyl pectin, said low methoxyl pectin being characterized in that the pectic acid units thereof contain from 2.5% to not more than 7% methoxyls per pectic acid unit, whereby the chill setting of such gelatin solutions is improved.

2. The method of claim 1 wherein the concentration of the gelatin is from 1.54% to 2.54% and the concentration of the low methoxyl pectin is of the order of up to 10% based on the dry weight of the gelatin.

3. The method of coating a cellulose acetate support which comprises preparing a solution of gelatin and low methoxyl pectin, said low methoxyl pectin being characterized in that the pectic acid units thereof contain from 2.5% to not more than 7% methoxyls per pectic acid unit, and then applying the solutions to said support at the rate of approximately two pounds of the solution per 100 square feet of support.

4. As a new article of manufacture a film support which carries on its surface a layer essentially comprised of gelatin, which gelatin contains low methoxyl pectin, said low methoxyl pectin being characterized in that the pectic acid units thereof contain from 2.5% to not more than 7% methoxyls per pectic acid unit.

5. A product in accordance with claim 4 wherein the

support is cellulose acetate and the content of low methoxyl pectin is not greater than 10%.

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