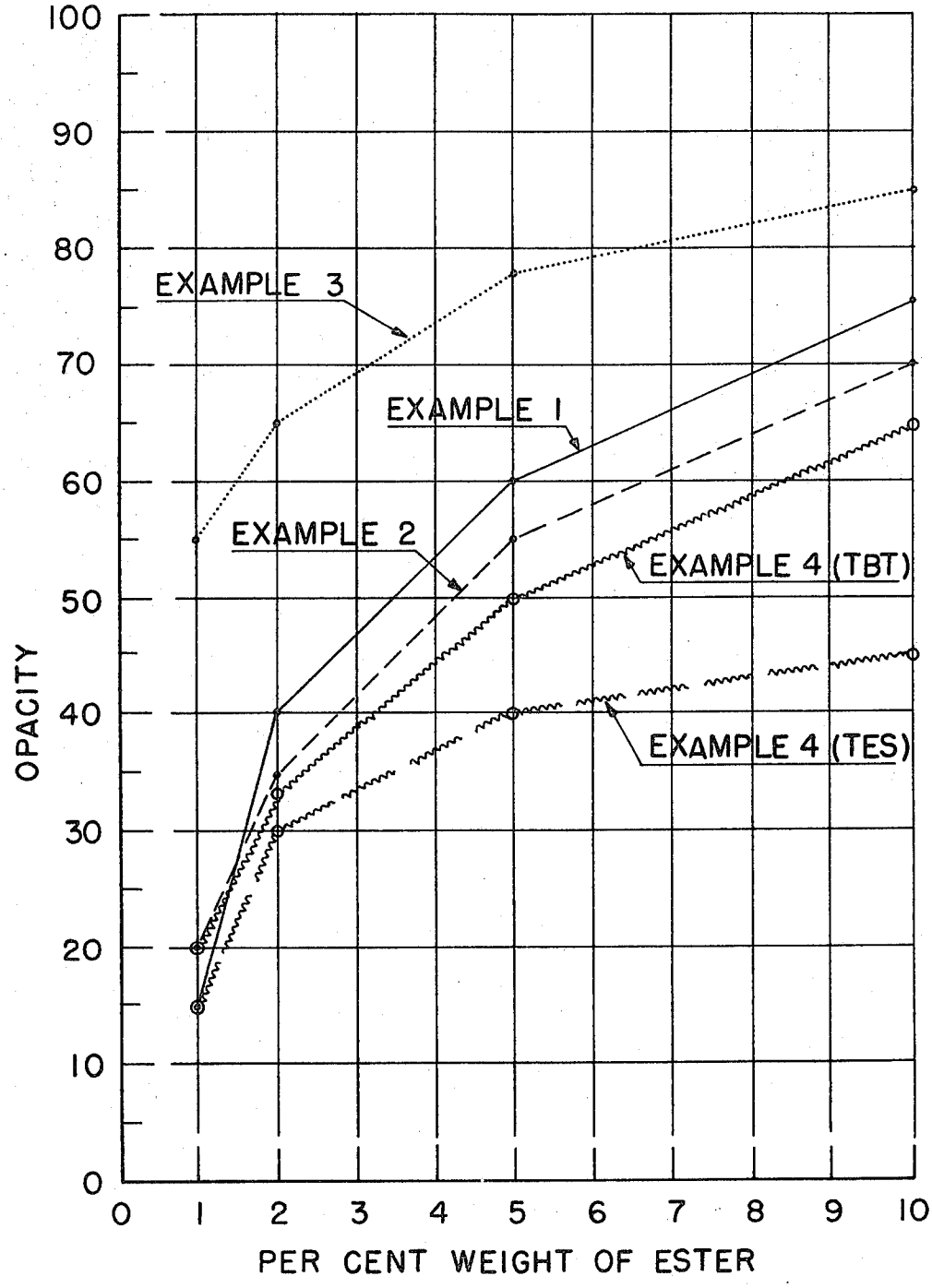
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METHOD FOR PRODUCING PAPER-LIKE POLYMER FILM AND THE PRODUCT

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METHOD OF PRODUCING PAPER-LIKE POLYMER FILM AND THE PRODUCT

Eckhard C. A. Schwarz, Neenah, Wis., assignor to Kimberly-Clark Corporation, Neenah, Wis.

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U.S. Cl. 260—41 B 14 Claims

ABSTRACT OF THE DISCLOSURE

Paper-like films are produced by extruding molten polystyrene or polystyrene/polyolefin mixtures with 1 to 20% based on the weight of the polymer or a hydrolyzable metal alkyl ester of titanium, silicon, or the like and orienting longitudinally in a heated water bath, then stretching laterally in the presence of steam. After drying, the film is opaque, paper-like, and receptive to conventional inks.

DESCRIPTION OF THE INVENTION

Paper has provided the basic substrate for written communications over a period of time extending back thousands of years. Although recent attempts have been made to produce materials to compete with paper for this market, such materials have met with limited success. The low cost of producing paper plus the responsiveness of the industry in adapting it to consumer needs have contributed largely to its success in dominating this market except for certain specialty items.

However, it is recognized that by virtue of our expanding population, alone, the demand for paper will ultimately exceed the capacity for its supply. This situation is presently approaching reality in a number of countries having a limited pulp supply. For example, in Japan vigorous efforts have been made to penetrate a market dependent upon imported paper materials, as it amply demonstrated by U.S. Pat. 3,515,567.

Furthermore, in other highly developed areas such as the United States the plastics industries have succeeded in reducing the cost of some materials to a point where they could become competitive with paper. These plastics generally have additional advantages in that they can be designed for higher wet and tear strengths as well as increased resistance to degradation over the same properties of paper generally. Also, plastic sheets may be opacified to the extent that when produced at a very thin gauge they still may receive writing or printing on both sides. This latter property presents obvious advantages for applications such as air mail letters where sheet weight is a significant factor.

A primary deterrent to the more rapid utilization of plastic writing surfaces is the fact that the materials which offer the best likelihood of cost competition are hydrophobic in nature and thus unreceptive to conventional inks. Numerous methods have been devised for rendering these plastic surfaces hydrophilic and printable, but it is a common characteristic of each of these methods that the cost of the resulting sheet is increased significantly. Examples of such methods include corona discharge treatment, described generally in U.S. Pat. 3,018,189; etching, described generally in U.S. Pat. 2,715,077; and graft polymerization, described generally in U.S. Pat. 3,382,090.

It is a primary object of the present invention to provide a synthetic sheet material capable of competing with paper for the market in substrates for written or printed indicia.

It is further an object to provide a method for producing at a low cost such a substrate material.

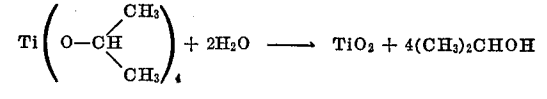
A related objective is to produce a synthetic sheet material that is generally hydrophilic for all purposes and uses for which hydrophilic sheets may be made suitable.

Other objects and advantages of the invention will become apparent upon reading the following detailed description and upon reference to the specific examples.

In the context of my invention the term "paper-like" is defined to include those structures generally having a thickness of from 10 to 200 microns, opacity (as measured by TAPPI Standard Method No. 175 P) of from 30 to 100 percent, and receptivity to conventional printing inks.

In accordance with the present invention these objectives are preferably attained by injecting a molten polymer with a hydrolyzable metal alkyl ester such as tetraisopropylorthotitanate, extruding the polymer through a film die, orienting it longitudinally in a water bath at 95°–100° C., and stretching it in a tenter frame in the presence of steam at 105°–140° C. The resulting product is opaque, has the feel of paper and is receptive to conventional inks.

While it is not intended that my invention should be limited to any particular theory or mechanism, it is believed that the inorganic ester is hydroyzed to the metal oxide which precipitates in the polymer structure as fine particles and acts as an opacifier. The resultant alcohol diffuses to the surface causing fine wrinkles of 0.1 to 50 microns in size, thus rendering the surface printable. The reaction based on this theory is as follows:



While the best opacity results were obtained with titanium esters, others such as those of silicon (e.g. tetraethylorthosilicate) also produce products having the aforementioned advantageous properties.

The following examples are included by way of illustrating my invention in detail. Proportions included herein are by weight unless otherwise noted. It is not intended that my invention be limited to these examples or in any manner except as indicated by the claims which conclude this disclosure.

EXAMPLE 1a

In this example, polystyrene (Styron 685 by Dow, having a melt flow of 2.4 g./10 minutes as measured in accordance with ASTM D–1238–62T) was extruded through a film die onto a chill roll to a film thickness of 180 microns. By means of a positive displacement pump, liquid tetraisopropylorthotitanate (TPT) was injected into the extruder barrel at a rate of 1%, 2%, 5%, and 10% of that of the polymer in terms of weight. This amounts to 0.3, 0.6, 1.5, and 3.0% TiO_2 after hydrolyzation of the TPT to TiO_2+isopropanol. The resulting films were fed through a roll system and stretched longitudinally in a water bath at 95° C. to 3 times their original lengths. Then they were stretched laterally to 3 times their widths in a tenter frame while heated by unsaturated steam at 120° C. The films then were dried while still in the tenter frame clamps by contact with air at 120° C. The final thickness of each of the films was 25 microns and the opacities (as measured by TAPPI Standard Method No. 175P) were 25%, 40%, 60%, and 75% in the order of increasing ester addition. The films were printable with conventional printing systems and possessed a paper-like feel and appearance. Films produced in the same manner but without the ester addition had an opacity of only 8% and lacked the stiffness and roughness characteristics of paper.

EXAMPLE 1b

In this example equivalent amounts of commercial anatase TiO_2 crystals were blended with the polymer to show that the results of my invention are not due to the simple addition of an opacifying agent. Thus, 0.03,

0.6, 1.5 and 3.0% by weight TiO_2 powder was blended with polystyrene flakes, and the mixtures were extruded through a film die to form films of 25 microns thickness. Opacities of these films were 12, 18, 26, and 39%, respectively. Comparison with the results of Example 1*a* shows that the TiO_2 generation in a film by "in situ" hydrolysis of a titanate ester like TPT provides much more effective opacification.

EXAMPLE 2

Example 1 was repeated, substituting for the polystyrene a mixture of polystyrene (Styron 685) and commerical isotactic polypropylene having a melt flow of 4.5 g./10 minutes ASTM D–1238–65T (Profax 6423) in a weight ratio of 1 part polystyrene per 5 parts of polypropylene. In this case the film was stretched 4 x both longitudinally and laterally, and the film gauge was adjusted to 320 microns to yield a final film of 20 microns thickness. In the order of increasing ester addition, the film opacities were 20%, 35%, 55%, and 70%. All sheets were printable by conventional printnig methods and had paper-like feel and appearance. Films without the ester added are smooth with low opacities of about 6–8%.

EXAMPLE 3

For this example the procedure of Example 2 was repeated using polystyrene and polypropylene in a weight ratio of 1 to 10, respectively. Also, crystalline anatase titanium dioxide was added to the polymer flakes before extrusion in the amount of 1 lb. TiO_2 per 10 lbs. resin mitxure to further increase the opacity. The resulting films had opacities of 55%, 65%, 78%, and 85% in the order of increased ester addition. Without the ester the film similarly loaded with TiO_2 had an opacity of 40%.

EXAMPLE 4

In order to demonstrate that other metal tetra-alkyl esters could be used in my invention, Example 2 was repeated again using, first, tetraethylorthosilicate (TES) and second, tetrabutylorthotitanate (TBT) in place of TPT. With TBT the results were opacities of 20%, 33%, 50%, and 65% in the order of increasing ester addition—about the same as resulted from the use of TPT. The opacities obtained with the silicate were correspondingly, 15%, 30%, 40%, and 45%—although somewhat lower, still the paper-like properties were attained to some degree.

Turning now to the drawings, the sole figure illustrates in graphic form the results obtained in the above examples. It is there demonstrated that the use of up to 10% of the esters in accordance with my invention consistently doubles the opacity obtained without them. Furthermore, as shown by Example 3, my invention may be used to enhance the effect of conventional opacifiers such as TiO_2.

While the invention has been described and illustrated by way of specific examples it is not to be limited thereto. As will be apparent to those skilled in this art various modifications and substitutions may be made without departing from the spirit and scope of my invention. For example, while TiO_2 is used as an opacifier in Example 3, other conventional opacifiers such as clay, diatomaceous earth, etc. may be utilized. Furthermore, other esters such as zirconates, aluminates, etc. may be substituted for the preferred compounds set forth in the examples. Also, the polymers and polymer mixtures suitable for my invention are virtually unlimited and include film-forming thermoplastic polymers of high tensile strength which do not themselves react or complex with the inorganic ester as well as those of the examples.

The relative proportions of ester added and polyolefin in the film composition are not critical and, in general, depend upon factors such as cost and degree of "paper-like" qualities desired. However, the range of from 1 to 20% ester based on resin weight is useful in terms of my invention with the range of from 2 to 10% being preferred.

It is further to be recognized that alterations may be made in the procedure set forth in the examples while still deriving the benefits of my invention. It is only necessary that the conditions be such as would support the reaction set forth above. For example, a preferred water bath of 95° C. has been recited, but the range from 25 to 100° C. is satisfactory. Likewise, lateral stretching in the presence of steam at 120° C. is set forth, but the range of 25 to 170° C. can be used. The drying step may be accomplished by conventional drying apparatus or even by simple exposure to ambient conditions although the procedure specified in the examples is believed to provide optimum results.

The degree of orientation in either direction involves a matter of choice so long as at least some orientation takes place to produce the desired stiffness and tensile strength. In general, orientation of from 1.1× to 7× in the longitudinal direction and from 1.1× to 5× in the lateral direction provide useful results while the ranges preferred are from 1.5× to 3× longitudinally and from 1.5× to 3× laterally.

As a paper substitute, the film of my invention will find many applications including bindings for children's books, catalogs, repair manuals, parts lists, and other publications subject to heavy wear or exposure to grease, oils, or dampness. Due to its inherent resistance to damage from the elements, it is ideal for maps, identification tags, labels, etc. Films produced in accordance with my invention may be printed by any conventional method on one or both sides with very good results, including, one, two, and four-color offset systems. Other uses based on inherent properties such as excellent dimensional stability, cleanability, fold strength, and resistance to most oils and greases, water, mildew, and rot will suggest themselves to one skilled in this art.

While my invention has been described with refrence to specific embodiments, it is defined by the claims which follow, and only limitations which are recited therein are intended.

I claim:

1. A method of producing a polymeric film having paper-like stiffness, opacity and receptivity to conventional printing inks comprising the steps of:

providing the polymer in a molten state; injecting into the polymer 1 to 20% based on the weight of the polymer of a hydrolyzable metal alkyl ester;

forming a film from the injected polymer; orienting the film longitudinally in a heated water bath;

orienting the film laterally in the presence of heat and moisture while maintaining its oriented length and drying the film wherein the above steps provide a minimum desired opacity.

2. The process of claim **1** wherein said polymer is selected from the group consisting of polystyrene and polystyrene-polyolefin mixtures.

3. The process of claim **1** wherein said hydrolyzable metal alkyl ester is selected from the group consisting of tetraisopropylorthotitanate, tetrabutylorthotitanate, and tetraethylorthosilicate.

4. The process of claim **1** wherein said film is formed by extrusion and said hydrolyzable metal alkyl ester is injected into the extruder.

5. The process of claim **1** wherein said longitudinal orientation takes place in a water bath at a temperature of from 95° C. to 100° C.

6. The process of claim **5** wherein said film is oriented longitudinally by stretching it from 1.1 to 7 times its original length.

7. The process of claim **1** wherein said lateral orientation takes place in the presence of unsaturated steam at a temperature of from 105° C. to 140° C.

8. The process of claim **7** wherein said film is oriented laterally in a tener frame by stretching it from 1.1 to 5 times its width prior to lateral orientation.

9. A process for producing films having paper-like properties of opacity, stiffness, and ink receptivity from a polymer selected from the group consisting of polystyrene and mixtures of polystyrene with one or more polyolefins comprising the steps of

heating the polymer to its molten state; extruding the molten polymer into a film while injecting into the extruder a hydrolyzable ester selected from the group consisting of tetraisopropylorthotitanate, tetrabutylorthotitanate, and tetraethylorthosilicate in the amount of from 1 to 20% based on the polymer weight;

orienting said film longitudinally in a water bath at a temperature of from 95° C. to 100° C. by stretching it from 1.1 to 7 times it's original length to produce in situ formation of a metal oxide;

orienting said film laterally in a tenter frame in the presence of unsaturated steam at a temperature of from 105° C. to 140° C. by stretching it from 1.1 to 5 times its width prior to lateral orientation; and drying said film.

10. The process of claim 9 wherein said drying step is accomplished in air at a temperature of about 120° C.

11. The process of claim 9 wherein said polymer is polystyrene.

12. The process of claim 9 wherein said polymer contains 0 to 100% polystyrene and 100 to 0% isotactic polypropylene.

13. The product of the process of claim 1.

14. The product of the process of claim 9.

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ROBERT F. WHITE, Primary Examiner

J. R. THURLOW, Assistant Examiner

U.S. Cl. X.R.

106—193, 300; 260—429.5; 264—210, 211, 234, 289

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,694,399 Dated September 26, 1972

Inventor(s) Eckhard C. A. Schwarz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Abstract of the Disclosure, line 3, "or" should read --of--;
Column 2, line 72, "0.03" should read -- 0.3 --;
Column 3, line 21, "printnig" should read -- printing --;
Column 3, line 31, "mitxure" should read -- mixture --.

Signed and sealed this 24th day of April 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents