PROCESS OF TREATING POLYOLEFIN-COATED PAPER

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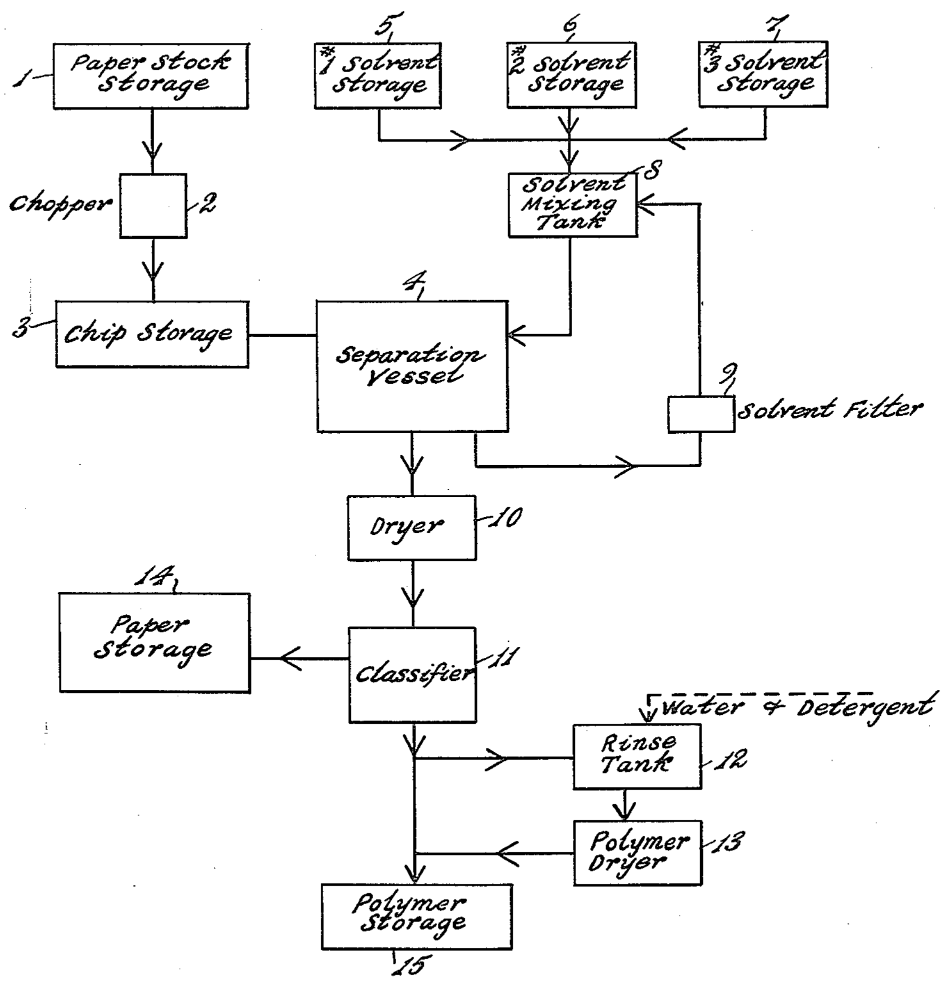

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The present invention relates to the process of treating polyolefin-coated paper to separate the polyolefin as an unmodified and unsupported film, from the paper, and more particularly relates to the economical recovery of "broke" waste generated in the process of coating paper with polyolefin, and the recovery of the waste of the finished paper product, as well as from its fabrication, all of which waste having a coating of polyolefin.

The present invention is a continuation-in-part of our copending application Serial No. 813,721, filed May 18, 1959, now abandoned, which in turn is a continuation-in-part of our copending application Serial No. 742,633, filed June 17, 1958, now abandoned, both for Process of Treating Polyethylene-Coated Paper.

When reference is made herein to polyolefin, it is intended to refer to the polyolefin containing from 2 to 4 carbon atoms in the carbon chain per monomer unit, examples being polyethylene, polypropylene, and any of the three polybutenes (1-butene, 2-butene or isobutene).

The recovery of the polyolefin coating makes the paper available and suitable as high grade paper stock and the polyolefin is useful in the plastic industry for a muliplicity of industrial purposes.

Wherever the reference is made herein to paper, unless otherwise indicated, it is used in its generic meaning and includes both what is called specifically paper and paper board as well as their products, and also includes all types deposited from a suspension of cellulose fibers. Throughout the disclosure the term polymer or polyolefin is frequently used to denote polyolefin having from 2 to 4 carbon atoms in the carbon chain.

The quantity of polyethylene used in the year 1958 in coating paper was 42,000,000 pounds.

Various methods of treatment of paper stock impregnated with wax, such as that shown in United States Patent 2,703,754, granted March 8, 1955, and others well known in the art, cannot be economically employed for the present purpose because the polyethylene employed in paper coating, where only commercially pure polyethylene is used, is definitely a resin and not a wax, although in the lower molecular weight ranges below 4000 it has some of the physical properties of wax.

For most practical coating of paper a molecular weight of polyethylene of about 19000 or greater is used, where resinous properties are distinctly exhibited. With the polyolefin of the type with which this invention is concerned, there is very little impregnation beneath the surface of the paper.

It is possible to recover some proportion of the paper fibers alone from the polyolefin without recovering the polyolefin, by simply "beating" the stock in the form of chips in water and then mechanically screening out the polyolefin fraction of the chips and recovering the paper fibers hydrated in a pulp. In this case the polyolefin fraction of the chips carries a considerable amount of paper fibers strongly adhering. With high grade paper board it is possible that the proportion of recoverable paper stock may be great enough to make such recovery economical, but in the case of stock classified as paper, as distinguished from paper board, the recoverable proportion is so little as to make the recovery doubtful. However, in both cases the polyolefin fraction of the chips is useless because of the difficulty of removing the adhering paper fibers. Polyolefin can be recovered from paper by chemical and thermal methods, by which the polyolefin coated chips are immersed in a hot solvent to dissolve all the polyolefin from the paper chips and then the polyolefin is precipitated by cooling and centrifuging. This procedure is difficult, however, and not economical, because at about the critical temperature range of 85 to 90 degrees C. and above, which is desirable for solution, the polymer has a tendency to gel.

A purpose of the present invention is to recover both paper stock and polyolefin coating in a simple direct manner, which overcomes the difficulty inherent in the prior process, and is characterized by relatively low cost and freedom from processing difficulties.

A further purpose is to recover substantially all the paper as suitable paper-making stock and a high percentage of the polyolefin available in a form which can be used and has a high market value.

A further purpose is to strip the paper completely of the polyolefin coating so that the coating separated from the paper has a wholly unsupported film with very little change in properties, retaining substantially no paper fibers clinging to the film.

The process of the present invention embodies the concept of bringing about a thorough separation of the coating from the paper so that the paper and the polyolefin retain their fixed form and identity without appreciably degrading and the polymer is not appreciably dissolved.

The ingredients of the solvent other than the alcohol and the water have strong solvent power for polyolefin at elevated temperature, both separately and together.

The alcohol in the mixture performs a complex function. The alcohol permits the solvent to swell and permeate the polyolefin coating but it limits the solubility of the polyolefin in the carbon disulfide and the chlorinated solvent or the like (compound of the second class) and effectively increases the polymer-to-solvent ratio, thus raising the critical solution temperature. Furthermore, the polar nature and the hydrogen bonding of the alcohol tends to swell the cellulose fibers, particularly at the elevated temperature. The carbon disulfide weakens the van der Waals forces which cause the adhesion of the polyolefin with the paper. The alcohol by encouraging differential swelling creates stresses between the polyolefin and paper, tending to cause the polyolefin to separate.

The alcohol further reduces the van der Waals forces. The chlorinated solvent or the equivalent acts synergistically to limit the solubility of the polyolefin in the carbon disulfide and promote the swelling and loss of adhesion.

Thus the dual swelling action of the solvent mixture on the polymer in juxtaposition, and the lessening of the bond, combined with heat and agitation cause the polyolefin film to shear off without attachment to the paper and without paper fibers clinging to it.

The indication of the swelling action is clearly shown by a matrix appearance which looks like fibers on the polymer film, after separation and drying, although in fact the actual fibers are no longer present.

The solvent mixture is made up of four necessary types of ingredients.

Carbon disulfide is the first important ingredient and its concentration should be in the range of 15 to 85 percent, preferably 25 to 40 percent and most desirably 33⅓ percent, all percentages being by weight.

The second ingredient is water miscible liquid monohydric or dihydric alcohol of the first class consisting of methyl alcohol, ethyl alcohol, normal propyl alcohol, isopropyl alcohol, tertiary butyl alcohol, allyl alcohol, propargyl alcohol, and ethylene glycol. Unsaturated alcohols are not preferred. The quantity of alcohol present should be between 5 and 50 percent, preferably between 25 and 40 percent and most desirably about 32⅓ percent by weight.

In addition it is important to include a liquid of the second class consisting of halogen substituted saturated and unsaturated straight and branched carbon chain compounds of a carbon chain length of between 1 and 6 carbon atoms, benzene, halogen substituted benzene, toluene, halogen substituted toluene, xylene, halogen substituted xylene and hydrogenated naphthalenes.

The quantity of the liquid of the second class present should be between 5 and 50 percent, preferably between 5 and 40 percent and most desirably 32⅓ percent by weight.

Specific examples of the compound of the second class are carbon tetrachloride, chloroform, methyl iodide, ethyl bromide, ethyl iodide, normal propyl bromide, isopropyl bromide, 1,1,2 trichlorethane, 1,2 dichloropropane, 1,2,3 trichloropropane, 1,6 dichlorohexane, 1,2,6 trichlorohexane, 1,2,4,6 tetrachlorohexane, 1,2,3,4,5,6 hexachlorohexane, mixed chlorohexane, methylene chloride, ethylene dichloride, trichloroethylene, tetrachloroethylene, benzene, monochlorobenzene, monobromobenzene, toluene, monochlorotoluene, monobromotoluene, xylene (ortho, meta or para), monochloroxylene, monoiodoxylene, tetrahydronaphthalene and decahydronaphthalene.

In addition to the above ingredients, the solvent should contain from 0.20 to 10 percent by weight of water, preferably from 2 to 5 percent, to protect against damage to the paper fiber.

The percentages of course will not add up to more than 100 percent, and the intention is that if a high percentage of one ingredient is used, the percentages of one or both of the other ingredients will be lowered so that the total will not be more than 100 percent.

The preferred alcohol to use with the carbon disulfide, with the liquid of the third class and with water is methyl alcohol or isopropyl alcohol. Of the compounds of the second class, the preferred is tetrahydronaphthalene, decahydronaphthalene, benzene, xylene, or toluene. Of the chlorinated compounds among the liquids of the second class, the preference is for carbon tetrachloride, tetrachlorethylene, chloroform and ethyl bromide.

The alcohols will commonly be used in a form containing 5 percent by weight of water, and this therefore is a convenient way of introducing the desired water. Up to 5 percent of water is normally found in ethyl, propyl and isopropyl alcohols.

The invention may be applied to treating high pressure type polyolefin and linear low pressure type polyolefin and to treating high density and low density polyolefin.

The polyolefin coated paper is desirably cut or chopped into chips having a size of from ¼ to 1¼ inches in either or both directions. The chip size is not critical, but chips of ½" x ½" have been found to be optimum. The chopped or cut paper is herein referred to as paper chips.

The paper chips are contacted with the solvent of the invention at temperatures of from 35 to 65 degrees C.

Operation at temperatures below 35 degrees C. is not satisfactory because of the limited permeation and swelling of the polyolefin film by the solvent mixture. Operation above 65 degrees C. causes complete solution of the polymer if agitation is present. The preferred range of temperature for operation is from 45 to 56 degrees C. and the best temperature is 50±2 degrees C. Very good results have been obtained at operating temperatures of 45 and 50 degrees C.

It will be evident that when performing the processes in a closed vessel at the temperatures referred to, the vapor pressures which result will build up pressures of between zero and twenty p.s.i. gauge.

The mixture of solvents and stock may be agitated by mechanical methods, either by introducing into the container a rotating agitator driven electrically, pneumatically, hydraulically, or by means of a steam or gas turbine, or by other suitable means, or by causing the vessel and contents to oscillate suitably at a frequency of 50 to 100 cycles per minute. The best agitation has been obtained by turbine wheel agitators at speeds of 700 to 750 r.p.m. The rotating agitators are generally preferred. The results obtained by ultrasonic agitation have not been favorable and it is not to be recommended except in special cases where metal foil is present on the paper chips.

The solvent-paper ratio is not critical and good results have been secured using solvent paper ratios between 5 to 1 and 15 to 1.

All of the following Examples I to VIII employ a sample of 10 grams (air dried) of paper chips coated with polyethylene, in each of the examples 100 grams of solvent was used.

Example I

At a temperature of 35 degrees C. the solvent and paper chips were stirred for thirty minutes, the solvent mixture being 15 percent carbon disulfide, 33 percent methyl alcohol, 50 percent carbon tetrachloride and 2 percent water by weight. Good stripping was obtained.

Example II

A sample of paper chips coated with polyethylene was stripped of polyethylene when agitated for 30 minutes by shaking the contents at 100 strokes per minute at a temperature of 55 degrees C. The solvent was 2 percent water and the balance equal weight proportions of carbon disulfide, methyl alcohol and carbon tetrachloride (32⅔ percent each).

Example III

At 50 degrees C. very effective stripping was obtained of polyethylene coating from paper chips using a solvent containing 3 percent of water and the balance equal weight proportions of carbon disulfide, carbon tetrachloride and ethyl alcohol (32⅓ percent each).

Example IV

Very effective stripping was obtained in 30 minutes at 50 degrees C. using a solvent containing 2 percent of water and the balance equal weight proportions of carbon disulfide, isopropyl alcohol and decahydronaphthalene (32⅔ percent each).

Example V

After 40 minutes stirring at a temperature of 35 to 45 degrees C. in a solvent containing 83 percent of carbon disulfide, 5 percent methyl alcohol, 10 percent carbon tetrachloride and 2 percent of water, the polyethylene coating was effectively stripped.

Example VI

After stirring for 40 minutes at 50 degrees C. in a solvent mixture consisting of 25 percent carbon disulfide, 23 percent of ethyl alcohol, 50 percent carbon tetrachloride and 2 percent of water, the polyethylene coating was effectively stripped.

Example VII

After stirring for 40 minutes at 45 degrees C. in a solvent mixture consisting of 2 percent of water and the balance equal parts by weight of carbon disulfide, ethyl alcohol and decahydronaphthalene (32⅔ percent each), the polyethylene coating was effectively stripped.

Example VIII

After exposure for 40 minutes at 45 degrees C. to a solvent mixture composed of 2 percent of water and the balance equal parts by weight of carbon disulfide, isopropyl alcohol and decahydronaphthalene the polyethylene film was effectively stripped.

Example IX

5 grams each of polypropylene coated bleached kraft paper and 5 grams of polypropylene coated unbleached

kraft paper were placed in separate flasks with a mixture weighing 90 grams of a solvent consisting of

32.33 percent isopropyl alcohol
32.33 percent carbon tetrachloride
33.34 percent carbon disulphide
2 percent of water

The percentages are by weight.

The temperature was maintained at 58° C. and the samples were agitated for thirty minutes. All samples were completely stripped of their coating of polypropylene by the end of the test and the polypropylene remained as flakes which did not dissolve but were separated from the paper.

All of the percentages given are by weight.

On completion of the stripping process there are two solids in the solvent liquid, the paper stock clear from the polymer coating and the polymer film, both in the form of chips, or in the case of the polymer, perhaps better called flakes.

The next step in the operation is to remove the liquid from the vessel and dry the solids. The polymers are intimately mixed with the paper chips. To separate paper chips from polymer flakes conventional classifying equipment based on difference in density and applicable to dry ingredients may be used.

In case there is evidence that fine paper fiber is clinging to the surface of the polymer flakes, aqueous rinse with a detergent is advisable.

Good results have been obtained in aiding the operation and reducing the difficulty in handling by eliminating or reducing static. This has been accomplished by introducing into the solvent from 1 percent to 10 percent, preferably 2 percent to 7 percent and most desirably 5 percent on the weight of the solvent of polyoxyethylene sorbitan monolaurate added for example to any of the examples herein.

In one preferred treatment the polyolefin coated paper is chopped to a chip size and immersed and agitated in a liquid solvent at an elevated temperature in the range from about 40 degrees C. to about 56 degrees C. with a solvent to stock ratio of 10 to 1 by weight. The solvent is a mixture of carbon disulfide, carbon tetrachloride and ethyl alcohol of approximate equal weight proportions, including 2 percent of water by weight. With the combined action of the solvent permeating and swelling the polyolefin and the paper at the interface, the bond of adhesion between the polymer and the paper breaks down and with agitation the polymer shears away from the surface of the paper.

The drawing shows a flow diagram useful in explaining the process.

The metallic equipment is conveniently made of carbon steel or cast iron, and stainless steel is not desirable because of the corrosion which it undergoes.

The polyolefin coated paper from stock pile **1** passes through a suitable chopping device **2** to provide paper chips of the desired size, which are stored in the paper storage **3**. From the paper chip storage the chips pass to the separating vessel **4**. The liquid solvents for the mixture are conveniently stored in three separate storage tanks **5**, **6** and **7**, the water normally being present in the alcohol. The solvents pass to a mixing tank **8**, where the liquid solvents are mixed, blended and heated to the required temperature and where the solvent mixture returned from the completed operation is stored. The heated mixture passes to the primary operation vessel **4** where it contacts the paper chips. In the vessel **4** the mass of chips is mechanically agitated by conventional means and the temperature range is maintained throughout a length of time adequate for complete separation, which will vary from 10 minutes to 25 minutes depending on the tightness of the bond of the polymer to the paper, the density of the polymer and the mixture used. In completion of the separation cycle, the remaining solvent is drained off and passed through filter **9** and then returnd to the solvent mixing tank. The separated paper chips and the polyolefin flakes are transferred to the dryer **10** and thence to dry solid classifying unit **11**. From the classifying unit the paper chips pass to storage **14**. The polyolefin flakes may if desired be washed with detergent **12** and then dried in polymer dryer **13** and passed to polymer storage **15**.

From the foregoing description, it is evident that the process of the invention provides a simple and economical method for the treatment of polyolefin coated paper. Both polyolefin and paper are recovered in commercially useful and valuable form. Considerable modification is possible in the process of the invention without departing therefrom.

Similar practical applications in accordance with the drawing can be made in treating polypropylene and polybutene coated papers as well as polyethylene coated papers.

In view of our invention and disclosure, variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of our invention without copying the process shown, and we, therefore, claim all such insofar as they fall within the reasonable spirit and scope of our claims.

Having thus described our invention what we claim as new and desire to secure by Letters Patent is:

1. The process of treating paper coated with a polyolefin having a monomer unit of the class consisting of etheylene, propylene, 1-butene, 2-butene and isobutene to separate said polyolefin as a film from the paper, which comprises immersing and agitating said polyolefin coated paper in the form of chips in a liquid composition at a temperature between 35° C. and 65° C., essentially consisting of a mixture of (1) carbon disulfide between 15 and 85%, (2) a water miscible liquid alcohol of a first class consisting of methyl alcohol, ethyl alcohol, normal propyl alcohol, isopropyl alcohol, tertiary butyl alcohol, allyl alcohol, propargyl alcohol, and ethylene glycol between 5 and 50%, (3) a liquid of a second class consisting of halogen substituted saturated and unsaturated straight and branched carbon chain compounds of a carbon chain length between 1 and 6 carbon atoms, benzene, halogen substituted benzenes, toluene, halogen substituted toluenes, xylene, halogen substituted xylenes and hydrogenated naphthalenes between 5 and 50% and (4) from 0.20 to 10 percent of water, said liquid composition operating synergistically to swell and permeate without dissolving the polyethylene and to swell the fibers of the paper, and break down the bond of adhesion between the polyolefin and the paper fibers, then removing said liquid composition from the paper and separate polyolefin film, and finally separating the polyolefin film and paper.

2. The process of claim 1, in which the temperature of treatment is between 40 and 56 degrees C.

3. The process of claim 1, in which the concentration of carbon disulfide is between 25 and 40 percent, the concentration of the compound of the first class is between 25 and 40 percent and the concentration of the compound of the second class is between 25 and 40 percent.

4. The process of claim 1, in which the concentrations of carbon disulfide, of the compound of the first class, and of the compound of the second class in the solvent are substantially equal.

5. The process of claim 1, in which the liquid composition is composed of carbon disulfide, methyl alcohol, carbon tetrachloride and water.

6. The process of claim 1, in which the liquid composition is composed of carbon disulfide, isopropyl alcohol, carbon tetrachloride and water.

7. The process of claim 1, in which the liquid com-

position is composed of carbon disulfide, isopropyl alcohol, decahydronaphthalene and water.

8. The process of claim 1, in which the liquid composition is composed of carbon disulfide, ethyl alcohol, decahydronaphthalene and water.

9. The process of claim 1, in which the liquid composition is composed of carbon disulfide, ethyl alcohol, carbon tetrachloride and water.

10. The process of claim 1, which comprises adding to the liquid composition from 1 to 10 percent of the weight of the solvent of polyoxyethylene sorbitan monolaurate.

11. The process of claim 1, in which the polyolefin is polyethylene.

12. The process of claim 1, in which the polyolefin is polypropylene.

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