Fig. 1.

CHIP FEED 20

STRIPPING TANK 21

MAKEUP 22

PREHEAT AND MIXING TANK 23

FERMENTATION TANK 24

SEPARATOR 28

CONDENSER 30

POLYETHYLENE CHIP RECEIVER 31

PAPER CHIP RECEIVER 26

VAPOR REHEATER 27

E. D. GROSSMANN ET AL. 3,051,610

PROCESS OF TREATING POLYOLEFIN-COATED PAPER

Filed Aug. 5, 1960

2 Sheets-Sheet 1
PROCESS OF TREATING POLYOLEFIN-COATED PAPER


Filed Aug. 5, 1960, Ser. No. 47,770

11 Claims. (Cl. 162—5)

The present invention relates to the process of treating paper coated with a polyolefin having from two to four carbon atoms per monomer unit to separate the polyolefin, as an unmodified and unsupported film, from the paper, and more particularly relates to the economical recovery of "broken" waste generated in the process of coating paper from polyolefin, and recovery of the waste of the finished paper product as well as the waste from its fabrication—all coated with polyolefin. Such recovery makes the paper available and suitable as high grade paper stock, and the polyolefin is useful also in the plastic industry for a multitude of industrial purposes.

The present application is a continuation-in-part of our copending application Serial No. 814,619, filed May 20, 1959, and now abandoned, for Process of Treating Polyethylene Coated Paper.

The present invention applies to treating of paper which is coated with polyolefins having from two to four carbon atoms per monomer unit in the carbon chain. These include polyethylene, propylene and polybutene. It will be evident, of course, that there are three polybutenes which are included. The monomers are frequently designated as 1-butene, 2-butene and isobutene.

A total of about 42,000,000 pounds of polyethylene was used in coating paper stock in 1958.

Where reference is made herein to paper, the term is used in its generic sense and includes both paper and paperboard as well as their products, and includes all types which are deposited from a suspension of cellulose fibers. Throughout this application where polymer or polyolefin is referred to it is intended to denote polyolefin having from two to four carbon atoms per monomer unit in the carbon chain.

The various methods of treating paper stock impregnated with wax, covered by patents such as U.S. Patent No. 2,703,754, granted March 8, 1955, as well as others known in the art, are distinctly different from the present invention. Polyethylene used for coating paper is a commercially pure resin and not a wax, and whereas in molecular weights below 4,000 it has certain physical properties similar to a wax, the polyethylene used in coating paper ordinarily has a molecular weight of 19,000 or above, and has distinctly resinous physical properties. With polyethylene of the type with which we are here concerned, there is very little impregnation of the paper below the surface.

It is possible to recover some proportion of the paper fibers separated from the polyolefin by simply heating the stock in the form of chips in water and then mechanically screening out the polyethylene and recovering the paper pulp. In this case, however, the polyethylene fraction of the chips carries a considerable amount of paper fiber strongly adhering to it.

Where the paper stock is high grade paperboard it is possible that the proportion of recoverable paper stock might be great enough to make such a process economical, but where the paper stock is of the character classified as paper rather than paperboard, the small portion recoverable makes the economy doubtful. In both cases, however, the value of the recovered polyolefin fraction is small or negligible because of the difficulty of removing the adhering paper fibers.

In case an effort is made to recover paper and polyolefin by chemical and thermal methods, suitably immersing the polyolefin in a hot solvent with the effect of dissolving out of the polyolefin from the paper chips, separating the solvent, and then precipitating the polyolefin by cooling and centrifuging, recovery is difficult because at about the critical temperature range of 85° C. to 90° C. required for solution, the polyolefin 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 difficulties inherent in the prior processes and which is characterized by relatively low cost and freedom from processing difficulties.

A further purpose is to recover substantially all of the paper from polyolefin coated paper as suitable papermaking stock and to recover a high percentage of the polyolefin in a form which can be reused and sold at a desirably high price.

A further purpose is to strip the paper completely from the polyolefin coating in such a manner that the coating separates as a wholly unsupported film with little or no change in its properties, and retains substantially no paper fiber clinging to the polyolefin film.

The present process contemplates bringing about a thorough separation of the coating from the paper so that the paper and the polyolefin retain their physical form and identity without appreciably degrading either the paper or polyolefin and without dissolving the polyolefin.

Solvents are used which except for the alcohol fraction have strong solvent power for polyolefin at elevated temperature both separately and together. The presence of alcohol in the solvent mixture permits the solvent to swell and permeate the polyolefin coating, lowering the strength of the van der Waals forces which tend to make the polyolefin adhere to the paper, but the alcohol limits the tendency of the other solvents present to dissolve polyolefin, and effectively increases the polymer-to-solvent ratio, thus raising the critical solution temperature.

Furthermore the polar nature and hydrogen bonding of the alcohol tends to swell the cellulose fibers at elevated temperature. Thus swelling occurs in both the paper and the polyolefin, but the effect occurs at different rates so that stresses are developed which cause separation of the paper from the polyolefin at the interface. Not only are van der Waals adhesion forces overcome, but mechanical shear stresses develop which separate the mechanical interlock between the polyolefin and the paper.

Thus, it will be evident that this dual swelling action of the solvent mixture on the polymer and paper in juxtaposition lessens the bond of adhesion between them, and with heat and agitation the polyolefin film shears off unattached to the paper, and without having paper fibers clinging to it.

The presence of the swelling action is clearly shown by a matrix appearance of fibers on the surface of the polymer film after separation and drying, although the actual fibers themselves are no longer present, and all one sees
is the contour which was produced when the fibers were present.

In our copending application Serial No. 742,633, filed June 17, 1938, for Process of Treating Polyethylene Coated Paper, we disclose and claim a solvent mixture which is based upon carbon disulphide. This is objectionable because the mixture of solvent has toxic, hazardous and corrosive properties derived from carbon disulphide that make the process difficult and more expensive to operate. By the process of the present invention, the toxicity, danger and corrosiveness of the solvent are greatly reduced. Furthermore, the cost of the plant for operation according to the improved process is only 55 to 58% as great as the cost of the plant for the process using carbon disulphide. Also, the operating cost is less because the cost of the improved solvent of the present invention is lower.

The solvent mixture according to the present invention is the mixture formed when the fibers were present in all cases includes four liquid substances. Caution should be noted at this point, because some of the solvents mentioned in the description below are gases at operating temperature and ordinary conditions of pressure, and if such solvents are to be used it will be evident that the pressure will be elevated to maintain all of the solvent in the liquid state. It will be evident, however, that it is preferable to use solvents which are normally liquids at the operating temperature, in which case the requirement of super-atmospheric pressure is eliminated.

The solvent mixture will contain a compound of the first class, preferably a material which can act as a solvent to weaken the van der Waals forces at the interface between the paper and the polyethylene.

The material of the first class will be a saturated hydrocarbon ring compound which is liquid under the operating conditions and which has between 3 and 8 carbon atoms inclusive in the ring, or a mono- or di-substituent thereof, decahydronaphthalene or tetrahydroprophthalene. Specific examples of the liquid solvent of the first group are cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, or the monomethyl or monoethyl derivatives of any of these, such as methylcyclohexane, decahydroprophthalene and tetrahydroprophthalene. Cyclopentane and cyclobutane will of course require super-atmospheric pressure as previously mentioned.

The preferred solvent of the first class is cyclohexane, and next to it the preference is for decahydronaphthalene.

The quantity of the liquid of the first class in the mixed solvent should be between 15 and 85%, preferably between 25 and 40% and most desirably about 32%, all percentages being by weight.

In addition to the solvent of the first class a solvent of the second class is included. This is a liquid monohydric or dihydric alcohol which is completely water miscible. As already explained, it aids in the swelling, it blocks a solubility of the polyethylene in the other solvents, and it cooperates to maintain miscibility with water which prevents damage to the paper fiber.

Specific examples of alcohols which may be used are methyl alcohol, ethyl alcohol, normal propyl alcohol, isopropyl alcohol, tertiary butyl alcohol, allyl alcohol, propargyl alcohol and ethylene glycol. Each one of these alcohols is completely miscible with water. The unsaturated alcohols are not preferred.

The quantity of the compound of the second class, the alcohol, in the mixture of solvent should be between 5% and 50%, preferably between 25 and 40% and most desirably about 32%, all percentages being by weight.

The preferred alcohols are methyl, ethyl and isopropyl.

The next important ingredient of the solvent is a halogen substituted saturated or unsaturated straight or branched carbon chain or aliphatic compound having a carbon chain length between 1 and 6 carbon atoms inclusive, or halogen substituted benzene, halogen substituted toluene or a halogen substituted xylene. When reference is made to halogen substituted it is intended to indicate that the substituent group is either chlorine, bromine, fluorine or chlorine, or silicon dioxide of the particular compound may have more than one kind of halogen as a substituent.

Specific examples are carbon tetrachloride, chloroform, methyl iodide, ethyl bromide, ethyl iodide, normal propyl bromide, isopropyl bromide, methylene chloride, 1,2,3,4,5,6 hexachloro-

hexane, mixed chloroalanes, trichloroethylene, tetra-

chloroethylene, monochlorobenzene, o-dichlorobenzene, monochlorotoluene and monochloroxylen. All of these materials must be below the limits according to the operating conditions.

The concentration of the solvent of the third class just mentioned should be in the range between 5 and 30%, preferably between 25 and 40% and most desirably about 32%, all percentages being by weight.

The preferred compounds of the third class are carbon tetrachloride, tetrachloroethylene, chloroform and ethyl bromide.

The solvent should also contain between 0.20 and 10% by weight of water, preferably 1 to 5% and most desirably about 2%. The water has the effect of protecting against degradation or other damage to the paper fiber.

A typical way to introduce the water is by using alcohols containing water.

It will be evident that these materials will effectively make up the entire liquid mixture, and their percentages will total to 100 percent.

The paper will be quite operative on both the regular high pressure type of polyethylene and also the linear low pressure type. It also works on high and low density polyethylene.

For best results the paper stock is cut or chopped into chips which have a size on each side of from ⅛ inch to 1½ inches. The size of these paper chips, however, is not critical.

The paper chips are brought into contact with the solvent mixture at a temperature in the range between 35° C. and 65° C. Operation below 35° C. is not satisfactory because of limited permeation and absorption of the polyolefin film by the solvent mixture. Operation above 65° C. is likely to cause complete solution of the polymer if agitation is present and is therefore definitely undesirable.

The preferred temperature range is from 45° to 56° C., very good operating temperatures being 45° and 50° C. For the best results the temperature should be 50±2° C.

It will be evident that even when all of the chemical ingredients are normally liquids, when operating a closed vessel at the temperatures mentioned, the pressure will be between 0 and 20 p.s.i. gauge.

The solvent paper-ratio is not critical, and good results have been obtained in solvent paper-ratio ranges between 5 to 1 and 1 to 1.

The mixture of solvents and the material to be treated may be agitated by standard mechanical methods, either by the use of a rotating agitator driven electrically, pneumatically, hydraulically, or by a suitable steam or gas turbine, or other means, or by causing the vessel and its contents to agitate or oscillate suitably at a frequency of the order of 50 to 100 cycles per minute. Rotary agitators are preferred.

Ultrasonic agitator has not proved to be very effective except in the case of polyolefin coated paper which involves a metal foil component.

Most effective agitation was obtained in turbine type agitators at 700 to 750 r.p.m., although propeller agitators were used somewhat less effectively.

The samples in Examples I to VII noted below each consist of 10 grams (air dried) of polyethylene coated paper chips and 100 grams of solvent.

**Example I**

A paper chip sample was stripped effectively of polyethylene by stirring at 35° C. for 30 minutes with a solvent mixture of about 30% of cyclohexane, 19%
ethyl alcohol, 50% carbon tetrachloride and 1% water by weight.

Example II
A paper chip sample was stripped of polyethylene when agitated for 30 minutes by mechanical shaking at 100 strokes per minute at a temperature of 55°C. In the presence of a solvent mixture containing one percent of water and the balance equal parts of cyclohexane, methyl alcohol and carbon tetrachloride, all proportions being by weight.

Example III
A sample of polyethylene coated paper chips was stripped of the polyethylene when shaken for 30 minutes in a solvent containing 1% of water by weight, and the balance equal quantities by weight of decahydro-naphthalene, isopropyl alcohol, and chloroform at a temperature of 50°C.

Example IV
A sample of polyethylene coated paper was stirred for 40 minutes at a temperature of 35°-45°C with a solvent composed of 84% of cyclohexane, 5% of methyl alcohol, 10% of carbon tetrachloride and 1% of water by weight.

Example V
A sample of paper chips was stripped of its polyethylene coating by stirring for 40 minutes at 50°C with a solvent mixture consisting of 35% of cyclohexane, 18% of ethyl alcohol, 45% of carbon tetrachloride and 2% of water by weight.

Example VI
The best results were obtained by treating a sample of polyethylene coated paper chips with a solvent mixture consisting of 33 1/4% of cyclohexane, 33 1/4% of isopropyl alcohol (containing 91% of the alcohol and the balance water) and 33 1/4% of carbon tetrachloride by weight. The polyethylene was removed efficiently by 30 minutes agitation at 50°C, and the solvent is of improved stability and low corrosive characteristics.

Example VII
Next to the last example, the best results were obtained by treating polyethylene coated paper chips for 30 minutes at 50°C with a solvent mixture consisting of the following: cyclohexane 33 1/4%; ethyl alcohol 95% alcohol and 5% water by weight 33 1/4%; carbon tetrachloride 33 1/4% by weight. This solvent mixture is very stable and of low corrosion properties, and very effective.

The following example, unlike Examples I to VII, is not directed to polyethylene coated paper.

Example VIII
In this case two different papers coated with polypropylene were tested, the characteristics of the respective papers being as follows:

(I) Sample description:
Natural 50 pound kraft paper unbleached
Natural 50 pound kraft paper bleached

(II) Solvent mixtures:
(A) Carbon tetrachloride (CCl₄), cyclohexane (C₆H₁₂), isopropanol (i-C₃H₇OH) 99%, balance water. One-third each by volume.

(B) Carbon tetrachloride (CCl₄), 2-nitropropane (C₂H₅CH(NO₂)CH₂), isopropanol (i-C₃H₇OH) 99%, balance water. One-third each by volume.

(C) Cyclohexane (C₆H₁₂), 2-nitropropane (C₂H₅CH(NO₂)CH₂), isopropanol (i-C₃H₇OH) 99%, balance water. One-third each by volume.

The polyethylene coated papers were cut into chips of approximately ½ x ½ inch. The sample size was from ½ to 1 gram.

Solvent mixture A was made up of equal quantities by volume of cyclohexane, isopropanol (containing 1% of water (weight)) and carbon tetrachloride.

Samples of the polypropylene coated paper were placed in 125 ml. ground glass topped flasks, along with a few pieces of 4 mm. glass tubing and approximately 100 ml. of the solvent mixture was added to each sample. The flask was agitated by hand and wrist motion while a stream of warm water (60° to 62°C) was pouring over the outside of the flask for a time of five minutes. The pieces of glass rod aided the agitation.

The samples were completely stripped in the time of five minutes. There was no evidence of solution of the polymer. The polymer swelled and loosened and when the polymer flakes were dried they came back to slightly less than their original size. The polymer was free from adhering paper fiber and the paper was free from adhering polymer.

Similar results to the above are obtained with paper coated with polybutene.

Any one of the other liquids of the first class can be substituted for the liquids of the first class in the examples given, and any one of the other liquids of the second class can be substituted for the liquids of the second class in the examples given, and any one of the liquids of the third class can be substituted for the liquids of the third class in the examples given. Furthermore, any desired mixture of different liquids of the first class can be used, and any desired mixture of different liquids of the second class can be used, and any desired mixture of different liquids of the third class can be used within the total concentration ranges set forth above.

On completion of the stripping process as above described, there are two different solids mixed with the solvent liquid. One is the paper stock cleared from the polymer coating, the other is the polymer film separated from the paper stock. Both the solids are in the form of chips, or in the case of the polymer it may be preferable to describe the material as flakes.

The next step in the process is to remove the liquid from the vessel containing the mass, and then dry both of the solids. The polymer flakes are intimately mixed with the paper chips. To separate the paper chips from the polymer flakes conventional classifying equipment for dry solids of different densities may be used. In case there is evidence of fine paper fibers clinging to the polymer flakes, a water rinse with a detergent is advisable.

Using the same procedure as for solvent mixture A, solvent mixtures B and C (containing 2-nitropropane) were applied to the polypropylene coated papers. There was no loosening of the polymer and no noticeable swelling after 6 to 10 minutes, with agitation warming to 50°C, and 48 hours soaking at room temperature gave no loosening of the polymer.

In one preferred treatment the polyolefin coated paper chopped to a suitable size to form chips, is immersed and agitated in a liquid solvent at an elevated temperature in the range between about 40° C. and 56°C. with a solvent to stock ratio of 10 to 1 by weight. The solvent is a mixture of cyclohexane, ethyl alcohol (95% balance water) and carbon tetrachloride, with approximately equal weights of each. With the double action of the mixture permeating and swelling both the polyolefin and the paper at the interface, the bond of adhesion breaks down by loosening the van der Waals forces and causing the development of stresses, and with agitation the polyolefin flakes shear off away from the surface of the paper.

In the drawings we illustrate apparatus which can be conveniently used in performing the process.

FIGURE 1 is a flow sheet in accordance with the invention.

FIGURE 2 is a diagrammatic illustration of an actual plant which can perform the process.

Referring first to the flow sheet of FIGURE 1, polyole-
fin coated paper from a suitable stockpile passes through a chopper and chips are fed by a chip feed 20 to a stripping tank which, along with other metal equipment, will preferably be of carbon steel or cast iron and preferably not stainless steel because stainless steel does not have favorable non-corrosive properties with the present solvent.

The solvent mixture of the character already described is supplied from a suitable makeup 22 (and also from fractionator 31 later described) to a preheating and mixing tank 23 from which it is introduced in proper proportions to the chip feed into stripping tank 21. After a suitable length of treatment in the stripping tank the free solvent is returned to the preheating and mixing tank by a suitable means 24. The mainly solid material from the stripping tank passes to dryer 25, from which paper chips are discharged to paper chip receiver 26. The dryer receives solvent vapor from vapor reheater 27.

Also from the dryer polyolen flakes and solvent pass to separator 28 from which solvent passes to vapor reheater 27 and also to condenser 30, and polyolen flakes pass to polyolen chip receiver 31. From the condenser 30 solvent passes to fractionator 31' which purifies the solvent and returns to the preheating and mixing tank 23.

As shown in FIGURE 2 polyolen-coated paper is reduced to chips at 32, placed in a stockpile 33, then passed through a suitable controlled feed 34 to a stripping tank 35 which contains a rotary agitator 36 and a heater coil 37 to maintain the preferred temperature previously mentioned.

Solvent in the proper quantity is brought into the stripping tank 35 by pump 38 from a solvent preheating and mixing tank 40 heated by a suitable heating coil 41. The solvent compounds are fed through suitable proportioning pump means to the solvent preheating and mixing tank from solvent storage tanks 42, 43 and 44.

Discharge from the bottom of the stripping tank 35 is accomplished through proportional worm drive feeder 45 which discharges into drying and classifying tower 46. From the top of the drying and classifying tower, solvent and polyolen flakes or chips pass to cyclone separator 47 and the polyolen chips pass to polyolen chip receiver 48 while the solvent passes to condenser 50 and condensate receiver 51 from which it is returned by fractionator feed pump 52 to fractionating tower 53 heated by heater coil 54 and passes to distillate condenser 55 and to reflux drum 56 from which suitable connections are provided to discharge waste and also to return solvent to the solvent preheating and mixing tank through pump 56'. Some of the solvent from the cyclone separator 47 also passes through solvent vapor reheater 57 to the bottom of drying and classifying tower 46.

From the bottom of the drying and classifying tower through worm drive conveyor feeder 58 the paper chips are discharged into paper chip receiving bin 60.

The time of treatment in the stripping tank may vary from 10 to 125 minutes depending upon the tightness of bond of the polymer to the paper, the density of the polymer and the mixture used.

The plant layout referred to above is suitable in separating polyproylene and polybutenes from paper, as well as polyethylene.

Tests have been carried on to determine whether the polymer flakes recovered are changed in any way by the process, and it has been found that in fact no change is accomplished as evidenced by infra-red spectra.

In operation, it will be evident that the process initially comprises preparation of the chips, preparation of the solvent, mixing together the chips and the solvent under proper conditions of temperature and treatment ratio, and then separation of the paper from the polyolen and recovery of the polymer.

In order to aid the separation of the paper chips and the polyolen chips when they are no longer adhering, it is desirable to reduce the static charge. This can most effectively be accomplished by adding polyoxyethylene sorbitan monolaurate (Twee 20).

The permissible range is between 1 and 10 percent of the total weight of the solvent, the preferred range is between 2 and 7 percent of the weight of the solvent and the most desirable range is about 5 percent of the total weight of the solvent. This permits the mechanical separator to operate more efficiently.

An example of a solvent including the static eliminator is the solvent of any one of the examples containing 1 to 10 percent of added polyoxyethylene sorbitan monolaurate.

From the foregoing description it is evident that the process of the invention is simple and economical. Both the polyolen and the paper are recovered in commercial form and are saleable. Considerable modification is possible in the process of the invention without departing from the scope thereof.

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 process shown, and we, therefore, claim all such insofar as they fall within the reasonable spirit and scope of our claims.

In view of the above, it is desired and as new and as due to secure by Letters Patent is:

1. The process of treating paper coated with polyolen having a monomer unit of the class consisting of ethylene, propylene, 1-butene, 2-butene and isobutene to separate the polyolen as a film from the paper, which comprises immersing and agitating the polyolen coated paper in the form of chips in a liquid composition at a temperature in the range from about 35° to about 65°C, said composition essentially consisting of a mixture of (1) a liquid of a first class consisting of saturated ring compounds having between 3 and 8 carbon atoms in the ring, single methyl substituents thereof, decahydronaphthalene and tetrahydronaphthalene between 15 and 85%; (2) a water miscible liquid alcohol of a second class consisting of methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, tert-butyl alcohol, allyl alcohol, propargyl alcohol, and ethyleneglycol between 5 and 50%; (3) a liquid of a third class consisting of halogen substituted benzines, halogen substituted toluenes and halogen substituted xylens between 5 and 50%; and (4) from 0.20 to 100% of water, said liquid composition operating synergistically to swell, saturate and permeate without substantially dissolving the polyolen, to swell the fibers of the paper, and break down the bond of adherence between the polyolen and the paper fibers, then remove said liquid composition from the paper and separate polyolen film and paper.

2. The process of claim 1, which comprises treating the chips with the liquid composition at a temperature between 45° and 56°C.

3. The process of claim 1, in which the concentration of the liquid of the first class, the liquid of the second class and the liquid of the third class is each approximately equal.

4. The process of claim 1, in which the concentration of the liquid of the first class is between 25 and 40%, the concentration of the liquid of the second class is between 25 and 40% and the concentration of the liquid of the third class is between 25 and 40%.

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

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

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

9. The process of claim 1, in which the liquid composition also contains between 1 and 10% of polyoxethylene sorbitan monolaurate.

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

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

References Cited in the file of this patent

UNITED STATES PATENTS

1,083,234  Werst  -----------------  Dec. 30, 1913
1,988,363  Snyder  -----------------  Jan. 15, 1935
1,993,362  Crisp  -----------------  Mar. 5, 1935
2,703,754  Myers  -----------------  Mar. 8, 1955

OTHER REFERENCES