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PAPERBOARD BASE IMPREGNATED WITH PITCH OR A BLEND OF PITCH AND HYDROCARBON POLYMER RESIN

John Podlipnik, Palos Heights, Ill., and Theodore J. Karr, Gary, and Eugene M. Fauber, Hammond, Ind., assignors to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

Paperboard is impregnated with mineral oil-derived pitch having a maximum needle penetration at 77° F. of about 125 and preferably between about 30 and 80. This impregnant may be obtained by solvent extraction alone or followed by blowing of clarified oil, that is, the bottoms produced from the catalytic cracking of mineral gas oil. The pitch product may also be blended with about 5–35 percent of a hydrocarbon polymer resin. The impregnated paperboard possesses improved wet and dry strength without leaving residual surface hydrocarbon.

This application is a continuation-in-part of application Ser. No. 343,447, filed Feb. 10, 1964, now abandoned.

This invention relates to an improved paperboard and its method of manufacture. In one embodiment, the present invention is directed to corrugated paperboard fabricated into the form of a box blank and impregnated with mineral oil-derived pitch.

It is well known in the art that waxes especially paraffin waxes obtained in the refining of petroleum, are used as impregnants for corrugated paperboard boxes to strengthen the board and to render them resistant to moisture. These wax-impregnated boxes are especially useful in the packaging of foods because the wax impregnant satisfies certain standards for purity and safety required by the Federal Food and Drug Administration of materials which come into contact with food. However, for packaging items other than foods, these governmental standards are not limiting and lower cost materials, especially from various petroleum fractions, may be used as impregnants.

To provide an acceptable corrugated paperboard product, the impregnant should not only strengthen the board and render it moisture resistant but it should also possess impregnating qualities that produce a uniform, completely impregnated paperboard free of surface residual that often causes blocking problems when corrugated boxes are stacked for storage. Petroleum fractions in general have heretofore proved unsatisfactory in that they usually fail to provide one or more of the desired characteristics. Asphalts, for example, although endowing paperboard with added strength and moisture resistance are too viscous and do not penetrate the paperboard readily at practical manufacturing temperatures. Likewise, other pitch-like materials such as coal tar, and high softening point (170–200° F.) air blown or heated clarified oil or thermal tar pitches are also too viscous to permit application by the dip-drain procedure.

It has now been found that a propane-insoluble pitch having a maximum needle penetration at 77° F. of about 125 which has been prepared from a mineral oil bottoms feed-stock obtained from the distillation of a cracked oil produced by catalytic cracking processes, is an excellent impregnant for corrugated paperboard. This pitch impregnates corrugated paperboard while leaving no surface residual and markedly improves the wet and dry strength of the paperboard.

The pitch of the present invention can be obtained by any suitable procedure, for instance, by solvent extraction or solvent extraction followed by blowing of bottoms derived from gasoline-producing catalytic cracking processes.

The cracked oil is the residual oil produced as a result of the cracking of a suitable mineral oil cracking feedstock such as petroleum gas oils, in the presence of catalysts such as silica-alumina crystalline aluminosilicates or other catalysts which are frequently in the fluidized state. In the distillation of the cracked oil, generally at about 7 to 25 p.s.i. pressure to a maximum or end point of about 650 to 750° F., to obtain gasoline and heavier distillates, there is produced a heavy residue or distillation bottoms containing entrained catalyst. To remove the catalyst, the residue is usually permitted to remain quiescent for a sufficient period of time to allow the catalyst particles to settle out, at which time the residue substantially free of catalyst may be decanted. In lieu of settling, the catalyst particles may be filtered or centrifuged from the oil, or such operations may be used in conjunction with settling.

In any case, there is obtained a clarified slurry oil, also referred to in the art as clarified oil. It is preferred that the clarified oil bottoms suitable for production of the pitch of the present invention boil primarily in the range of about 400 to 1000° F. and have a 5 volume percent distillation point of at least about 450° F. or even at least about 600° F. and a 95 volume percent distillation point of at least about 800° F., and with at least 100° F. or even at least about 200° F. units separating the 5% distillation point and the 95% distillation point. The clarified oil feed to be treated to provide the pitch of the present invention can be the full range clarified oil, that is, the entire bottoms obtained as aforementioned by the distillation of the oil from the cracking unit or it can be suitable bottoms fractions of the full range clarified oil, for example, a bottoms fraction having a 5 volume percent distillation point of below about 700° F. obtained, for instance, by vacuum distillation of the clarified oil to about 50%, and usually not less than about 25% bottoms. It is preferred that the cracking unit from which the clarified feed is obtained be operated at at least 50% conversion. Also, for reasonable yields of pitch, it is preferred that the clarified oil feed have an API gravity at 60° F. of up to about 25.

The clarified oil is selected and suitably treated to provide a pitch product having the desired viscosity and a maximum needle penetration at 77° F., 100 grm./5 sec. (ASTM-D-5) of about 125, preferably between 30 and 80. The specific gravity often will be about 1.0500 to 1.2200 and the softening point will preferably be about 110° to 125° F. In order to facilitate application the pitch may be prepared so as to possess a maximum Brookfield viscosity of about 50 centipoises and preferably from 15 to 35, at 275° F. However, in the event the viscosity of the pitch is higher than is desired for impregnation purposes, the pitch may be cut back to more suitable viscosity with a hydrocarbon solvent, for instance an aromatic solvent such as toluene. It is an advantage of the product of the present invention that unlike asphalts which are sufficiently hard to be used satisfactorily as impregnants, our product is completely soluble in numerous aromatic solvents with which it may be cut back.

In using solvent extraction to provide the pitch of the invention, an upper extract phase containing solvent and deasphalted oil is produced along with the raffinate or bottoms phase containing the pitch. Separation of this upper phase provides the pitch, usually after solvent in the raffinate is removed. Solvents suitable for use in the extraction include, paraffin hydrocarbons such as the lower alkanes, for example, C₃ to C₅ paraffins, especially normal paraffins, with propane being preferred. Any solvent remaining in the separated pitch can be removed by

simply heating at an elevated temperature, generally about 300° F., for a few minutes. The solvent to oil ratios and temperatures employed in the extraction may vary depending, for example, on the boiling range of the clarified oil feed, but in any event are selected to provide a pitch product having the desired properties. Generally, the solvent to oil volume ratios employed in the extraction will fall in the range of at least about 2:1, for example, about 3 to 15:1, and the temperature utilized for the extraction will often range from about 130° F. to 200° F. Although a single extraction may provide the desired pitch, a number of extractions may be employed. Ordinarily the solvent extraction conditions are those which reduce the clarified oil to at least about 5% bottoms or raffinate, generally about 5 to 50% bottoms, based on the full range clarified oil. In cases where a select bottoms fraction of the full range clarified oil is solvent extracted, the percent bottoms from the extraction, based on the select fraction may of course be greater than 50%, and may be up to about 85% or more. The extraction is preferably conducted in a manner that provides bottoms based on the full range clarified oil of about 10 to 20%.

Alternatively, blowing of an intermediate pitch with an oxygen-containing gas may be used subsequent to the solvent extraction procedure just described to obtain the impregnant. This procedure has the advantage that it permits termination of the solvent extraction when penetration values of above about 125 to 300 at 77° F. are reached rather than requiring that this process be continued until a pitch is extracted having a penetration of about 125 or less. If desired, the solvent extraction can be controlled to get a product of less than about 125 penetration before blowing. In any event, following extraction, the pitch may be blown, e.g. with air, in order to obtain any desired further decrease in penetration, for instance, at least about 25% or at least about 50% decrease to give a pitch having a penetration of less than about 125 and preferably from about 30-80 at 77° F. If desired, the blowing may be continued until a 0 penetration at 77° F. is reached and the pitch then cut back using suitable aromatic hydrocarbons until the proper viscosity is reached. Blowing can be carried out at temperatures of 350-550° F. and with air being introduced at a rate of 1-4 cubic feet per pound of material being treated. The rate of hardening, i.e. decrease in penetration, is dependent on the rate at which air is supplied during the process. Therefore, the lower the rate at which the air is supplied, the longer it will take to reach the desired penetration.

The base sheet material impregnated with the clarified oil pitch of the present invention can be any suitable paperboard but is preferably corrugated paperboard. In perhaps its most practical aspect the corrugated board can be impregnated in the form of a blank which will ultimately be erected into a corrugated box. Ordinarily corrugated paperboard is composed of a crimped medium having flat liners adhered to the crests of the crimped or corrugated medium. Application of the impregnant of the invention can be effected by any means known to the art, for example, by spraying, roll coating or the dip-oven drain procedure. The impregnant can be applied to the medium and/or liners separately prior to lamination of the paperboard on a corrugator machine or the impregnant can be applied after lamination, i.e. on the finished corrugated board. The impregnation is conducted in a manner that provides the paperboard sheet material with significantly greater rigidity which often takes at least about 15%, preferably at least about 25%, of the pitch impregnant of the invention, and most preferably about 50 to 80%, based on the total weight of the impregnated sheet material.

The superiority of the pitch of the present invention over other conventional impregnating materials is particularly evident, however, when the dry-oven drain procedure is employed for applying the impregnant. In this

procedure, the finished corrugated paperboard is dipped into a bath of the impregnant, usually for about 5 seconds to 5 minutes at an elevated temperature, generally about 200 to 300° F., after which the impregnated board is placed in an oven and dried at an elevated temperature, for instance, about 225 to 350° F., to remove excess impregnant. The heat treatment ordinarily lasts about 2 to 30 minutes after which the impregnated board is cooled at room temperature.

If desired, minor amounts of other resinous materials which improve the wet and dry strength of paperboard can be blended with the clarified oil pitch, and the blend employed as the impregnant. Suitable components are, for example, hydrocarbon polymer resins having an ASTM ring and ball softening point of above about 150° F., for instance, up to about 275° F. Particularly preferred are hydrocarbon polymer resins having as a repeating unit an aliphatic monocyclic terpene radical and a softening point as described above. Examples of the latter resins are polyterpene resins (Piccolyte Resins) and polydiene resin (Piccopale Resins). The polyterpene resins can be made by the acid catalyst polymerization of β -pinene and the polydiene resins by the acid catalyst polymerization of aliphatic dienes such as isoprene, with or without small amounts of other lower molecular weight olefins. β -pinene, although a bicyclic terpene appears to lose one of its two ring structures during polymerization to give the repeating terpene radical unit. In the polydiene resin formation, the non-cyclic diene starting material undergoes cyclization to the terpene radical. Both types of resins are non-aromatic, being essentially saturated or containing essentially a single double bond in the terpene radical. The average molecular weight of suitable resins will generally fall in the range of about 500 to 2000, often about 800 to 1400.

If employed, about 5 to 35%, preferably about 10 to 25% by weight based on the blend, of the additional terpene-type resinous component is generally blended with about 65 to 95%, preferably 75 to 90% by weight of the clarified oil pitch of this invention. Blending of the two components can be easily effected by heating at an elevated temperature, such as about 180° to 250° F. or more.

The following examples are included to further illustrate the present invention.

Example I

A clarified oil having a Saybolt Universal Viscosity at 210° F. of 42 seconds, an API gravity at 60° F. of 13.6° and having 5% and 95% distillation points of 600 and 935° F., respectively, was distilled by steam vacuum distillation to a 50% bottoms fraction. This 50% bottoms fraction was then extracted with propane using a propane to oil ratio of 7 to 1. The extraction was made by mixing the clarified oil bottoms fraction with the propane in a closed batch treating kettle for 30 minutes at 190° F. The mixture was permitted to settle for 3 hours until two separate phases were obtained. The bottom phase containing the pitch-like material which is the desired impregnant, was then separated from the upper phase containing the deasphalted oil. The small amount of propane contained in the pitch was then removed by heating for a few minutes at 300° F. The pitch obtained tested as follows:

Specific Gravity 77/77, ASTM D-70	1.1557
Softening Point (R & B), ° F., ASTM D-36	115.5
Saybolt Universal Viscosity at 210° F., ASTM D-88	977
Brookfield Viscosity at 275° F., centipoise	21
Needle Penetration at 77° F., ASTM D-5	48

The clarified oil pitch described above was evaluated as an impregnant for corrugated paperboard by immersing tared 4" x 6" panels of corrugated boards (C flute-130 lbs./1000 ft.²) into a bath of the pitch maintained

at 275° F. for 15 seconds. The corrugated board panels were then removed from the bath, allowed to drain at room temperature for 5 minutes, and were then subjected to a heat treatment by placing them in a forced draft air oven maintained at 275° F. for 20 minutes. After the heat treatment the impregnated paperboards were allowed to cool to room temperature and were weighed. The weight of the impregnant in the paperboard was determined by the difference between the tare weight and the final weight of the paperboard. This increased weight of the paperboard is a measure of impregnant consumed and is expressed as the percent weight increase based on the original weight of the paperboard.

Improvements in water resistance of the corrugated paperboard specimens impregnated with the clarified oil pitch were determined by measuring their crushing and bending strengths on the Instron Tensile Tester. These tests were made after soaking the impregnated paperboard specimens for 18 hours in water maintained at 78° F. The results were compared to crush and bend test results obtained on untreated paperboard specimens which were also soaked in water for 18 hours. In addition, crush and bend strength results were obtained on corrugated board specimens impregnated with a 50% bottoms fraction obtained by vacuum distillation of a full range clarified oil, a 200 to 300 penetration grade asphalt, and a thermal tar. The physical properties of these latter materials were as follows:

	50% Bottoms Fraction from Clarified Oil	200-300 Pen Asphalt	Thermal Tar
Gravity, °API.....	6.1		
Specific Gravity, 77/77.....		0.9975	1.0843
Viscosity, SUS/210° F.....		5,668	34.7
Penetration at 77° F.....	>125	217	(1)
Softening Point (R & B), ° F.....	<125	103	(1)
Viscosity, Centipoise at 275° F.....	7	163	4

¹ Fluid at 77° F.

Crushing strength was measured by crushing the impregnated 4" x 6" corrugated board specimens between two steel plates which were mounted in a steel cage to prevent any sliding movement when the load was applied. This minimized shear effects. The testing was done with either the D cell (1000 lb. max.) or the E cell (5000 lb. max.) using a chart speed of 2 inches per minute and a crosshead speed of 0.5 inch per minute.

The bending strength was determined by utilizing a special apparatus which forces the paperboard specimen to bend when a force is applied to a bar across the center of the specimen. The 4" by 6" specimen is held in place by two stationary bars set 3½" apart. The specimen is placed on the stationary bars so that the flutes in the paperboard are perpendicular to the bars. The crosshead speed on the Instron Tensile Tester was set at 5 inches per minute and the D cell (1000 lb. maximum) was used. The results of the tests are shown in Table I.

The test results in Table I show that corrugated paperboard impregnated with the clarified oil pitch has a crushing strength of 200 lbs. and a bending strength of 4.8 lbs. after being soaked in water for 18 hours. An untreated paperboard specimen, on the other hand, has no wet strength after a like period of soaking in water. In fact, the untreated paperboard specimens become soft and disintegrate readily after being soaked in water. Also, a dry untreated paperboard has a crush strength of 750 lbs. and a bend strength of 18 lbs. compared to a crush strength of 1225 lbs. and a bend strength of 32 lbs. after impregnation with the clarified oil pitch. These results show that the clarified oil pitch improves the strength of the paperboard and also waterproofs the paper. Besides these improvements in strength and resistance to moisture, the clarified oil pitch completely impregnates the paperboard with no surface residual which may cause blocking problems when corrugated paperboard boxes are stacked in storage.

The test results for the other materials demonstrate that other asphaltic materials including a conventional 200-300 penetration grade will not provide the desired properties. The data for the 50% bottoms clarified oil fraction show that while this fraction improves wet strength it does not improve strength of the dry board. Furthermore the wet strength improvement is considerably less than obtained with the propane treated material. This difference is due, at least in part, to the greater hardness and strength of the propane prepared product. Similarly, the softer, more oily thermal tar does not greatly improve wet strength properties. The 200-300 penetration grade asphalt affords considerably improved wet strength but, because of too high viscosity, much of the asphalt remained on the surface. This surface coat is somewhat tacky and leads to blocking or sticking together of the coated board.

Example II

A petroleum-derived clarified oil having a Saybolt Universal Viscosity at 210° F. of 43 seconds and an API gravity of 13.6° was extracted using a propane to oil ratio of 12.1 to 1. After settling, the bottom phase containing the intermediate pitch-like material was separated from the upper phase containing the deasphalted oil. The small amount of propane contained in the pitch was removed by heating for a few minutes at 300° F. The pitch obtained had a viscosity at 210° F. of 511, a needle penetration at 77° F. of 127, a softening point of 105° F. and a specific gravity 60/60 of 1.1624.

This pitch was then air blown at 500° F. and at a rate of 3.3 cubic feet of air per pound of pitch per hour. Samples were tested after 2½ and 4½ hours of air blowing with the following results observed.

TABLE I

Impregnant ¹	Percent Gain in Weight ²	Wet Strength, ³ lbs. per 4" x 6" Specimen		Dry Strength, lbs. per 4" x 6" Specimen		Description of Impregnated Paperboard
		Crush Test	Bend Test	Crush Test	Bend Test	
Propane Extracted Clarified Oil Pitch.....	71.0	200	4.8	1,225	32.0	Completely saturated paperboard, no surface residual.
50% Bottoms Fraction From Clarified Oil (obtained by vacuum distillation).....	55.5	85	2.0	775	19.3	Do.
200-300 Penetration Grade Asphalt ..	67.1	130	3.2	-----	-----	Little or no impregnation of paperboard, heavy surface residual.
Thermal Tar.....	60.5	58	1.8	-----	-----	Completely saturated paperboard, no surface residual.
Untreated Paperboard.....		0	0	750	18.0	

¹ Paperboard impregnated by dipping into impregnant at 275° F. for 15 seconds, followed by 5 minute drain at room temperature and heat treated for 20 minutes at 275° F. in forced draft air oven.

² Gain in weight divided by weight of untreated paperboard and multiplied by 100.

³ Determined after soaking specimens for 18 hours in water maintained at 78° F.

	At 2½ hrs.	At 4½ hrs.
Softening Point (R & B), ° F.	121	165
Specific Gravity, 60/60.	1.1780	1.1930
Flash, ° F.	485	510
Brookfield Viscosity, cps. at 300° F.	22.6	54.6
Brookfield Viscosity, cps. at 325° F.	15.8	1
Brookfield Viscosity, cps. at 350° F.		21
Needle Penetration at 77° F.	49	176
Needle Penetration at 115° F.		
Viscosity at 275° F., SSF		

These pitches are suitable for use as the impregnant of the present invention.

Example III

In accordance with the method of Example I, 4" x 6" corrugated specimens were impregnated with the clarified oil pitch of Example I containing 10, 20 and 30% respectively of petroleum polymer resin having an ASTM ring and ball softening point of about 212° F. The resin is commercially available and is essentially a hydrocarbon produced by the polymerization of unsaturates derived from the cracking of petroleum. Crush and bend tests were conducted on the impregnated specimens in Example I. Tests on an unimpregnated specimen and the specimen of Example I impregnated with clarified oil pitch are included for comparison. The results are tabulated in Table II.

TABLE II

Wt. Percent Polymer Resin in Clarified Oil Pitch	Consumption, crush, and bend test results on 4" x 6" corrugated paperboard impregnated ¹ with blends of propane extracted clarified oil pitch and polymer resin					Description of Paperboard Specimen
	Consumption, Percent Gain in Weight ²	Dry Strength, lbs. per 4" x 6" Specimen		Wet Strength, ³ lbs. per 4" x 6" Specimen		
		Crush Value	Bend Value	Crush Value	Bend Value	
10.....	66.8	1,370	36.9	212	5.3	Completely saturated, no surface residual.
20.....	68.3	1,595	44.5	282	6.5	Do.
30.....	69.5	1,705	46.2	358	9.5	Completely saturated, trace surface residual.
Untreated Paperboard.....		750	18.0	0	0	
Paperboard Impregnated with Propane Extracted Clarified Oil Pitch.	71.0	1,225	32.0	200	4.8	Completely saturated, no surface residual.

¹ Paperboard impregnated at 275° F. for 15 seconds, drained at room temperature for 5 minutes, and heat treated at 275° F. for 20 minutes in a forced draft air oven.

² Percent gain in weight based on untreated 4" x 6" specimen.

³ Determined after soaking in water at 78° F. for 18 hours.

As shown by the test results, the corrugated paperboard specimens impregnated with the clarified oil pitch containing 10, 20 and 30 weight percent of the resin, respectively, exhibit higher wet and dry strengths as measured by the crush and bend tests than those impregnated with the straight clarified oil pitch. Moreover, consumption and impregnating ability are not adversely affected.

What is claimed is:

1. An article of manufacture comprising a paperboard base impregnated with propane-insoluble pitch, having a maximum needle penetration at 77° F., of about 125 derived from mineral oil bottoms feedstock produced from the catalytic cracking of gas oil, said feedstock boiling primarily in the range of about 400 to 1000° F. and having a 5 volume percent distillation point of at least about 450° F. and a 95 volume percent distillation point of at least about 800° F.

2. The article of manufacture of claim 1 wherein the pitch impregnant has a needle penetration at 77° F. of about 30 to 80.

3. The article of manufacture of claim 2 wherein the pitch impregnant has a Brookfield viscosity at 275° F. of about 15 to 35 centipoises and a softening point of about 110 to 125° F.

4. The article of manufacture of claim 1 wherein the paperboard is corrugated paperboard.

5. The article of manufacture of claim 3 wherein the paperboard is corrugated paperboard.

6. An article of manufacture comprising a paperboard base impregnated with a blend consisting essentially of about 5 to 35% by weight of a hydrocarbon polymer resin having as a repeating unit an aliphatic hydrocarbon monocyclic terpene radical and a softening point of about 150° F. to 275° F. and about 65-95% by weight of a propane-insoluble pitch, having a maximum needle penetration at 77° F., of about 125 and a maximum Brookfield viscosity at 275° F. of about 50 centipoises, derived from a petroleum bottoms feedstock produced from the catalytic cracking of petroleum gas oil, said feedstock boiling primarily in the range of about 400 to 1000° F. and having a 5 volume percent distillation point of at least about 450° F. and a 95 volume percent distillation point of at least about 800° F. with at least about 100° F. units separating the 5 volume percent distillation point and 95 volume percent distillation point, said blend being at least about 25% of the total weight of the impregnated paperboard base.

7. The article of manufacture of claim 6 wherein the blend contains about 10 to 25% by weight of said hydrocarbon polymer resin.

8. The article of manufacture of claim 1, wherein the propane-insoluble pitch is derived from the mineral oil

bottoms feedstock by solvent extraction with a C₃ to C₅ paraffin.

9. The article of manufacture of claim 1 wherein the propane-insoluble pitch is derived from the mineral oil bottoms feedstock by solvent extraction with a C₃ to C₅ paraffin and followed by air blowing.

10. The article of manufacture of claim 9 wherein the pitch has a softening point of about 110 to 125° F.

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