United States Patent Office 3,467,547 Patented Sept. 16, 1969

3,467,547

CORRUGATED PAPERBOARD HAVING IMPROVED WET STRENGTH PROPERTIES

Wildon T. Harvey, Hockessin, Del., and Jay C. Knepper, Jr., Princeton, N.J., assignors to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

No Drawing. Continuation-in-part of application Ser. No. 374,835, June 21, 1964. This application July 6, 1967, Ser. No. 651,365

Int. Cl. D21h *1/22*; C09d *3/40*

U.S. Cl. 117—158 2 Claims

ABSTRACT OF THE DISCLOSURE

An improved wet strength corrugated paperboard composition comprising corrugated paperboard impregnated with 25 to 50 weight percent of a specific petroleum paraffin wax containing 0.1 to 1.0 weight percent of a synthetic oil produced by the Friedel-Crafts condensation of aromatic compounds and chlorinated paraffins.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. patent application Ser. No. 374,835, filed June 21, 1964, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the improvement of the wet stiffness characteristics of corrugated paperboard boxes. More particularly, this invention relates to an improved corrugated paperboard composition which comprises corrugated paperboard impregnated with a wax-synthetic oil composition.

For many years corrugated paperboard used in box manufacturing has been made with a bituminous layer interposed between intermediate plies of the sheet in order to render the corrugated paperboard resistant to water vapor transmission. This has provided paperboard which is relatively impermeable to water vapor transmission and is inexpensive to manufacture.

However, this type of corrugated paperboard has been found to be lacking in wet strength properties necessary for stacking, especially when in direct contact with water or when exposed to a moisture-laden atmosphere for prolonged periods of time. This loss of wet strength is attributed to moisture absorbance of the outer unprotected surfaces of the paperboard.

Waxes have long been used in coating paper, cloths, fibers, food, and corrugated paperboard products to render them moisture-vapor resistant. However, it has been found that unmodified waxes have a tendency to crack and peel. This disadvantage is overcome to some degree by addition of polyethylene and other polymers and copolymers. However, the expense, the high temperatures necessary for blending such mixtures, and the relative incompatibility of some of these polymer additives are disadvantages of these compositions in corrugated paperboard applications.

DESCRIPTION OF THE INVENTION

The present invention provides a paperboard for use in corrugated boxes which has all of the attractive properties of more expensive compositions and yet is relatively inexpensive to manufacture because of the low concentration of additive necessary to achieve the desired effect. It is among the objects of this invention to provide an inexpensive wax-synthetic oil composition to render corrugated paperboard relatively impermeable to water and thereby improve the wet strength of the corrugated paperboard. It is among the objects of this invention to provide an improved corrugated paperboard composition comprising a base corrugated paperboard impregnated with a thermoplastic homogeneous mixture of 99.0 to 99.9 percent mineral wax and 0.1 to 1.0 percent of a synthetic oil obtained by a Friedel-Crafts condensation of a chlorinated paraffinic compound and an aromatic compound, with said thermoplastic mixture comprising 25 to 50 weight percent, preferably 35 to 45 percent, of the corrugated paperboard composition.

The synthetic oils used in this invention can be made by various methods, but one of the most important methods used heretofore comprises the condensation of long-chain aliphatic compounds (e.g., containing more than 10 carbon atoms) with aromatic ring compounds by means of a Friedel-Crafts catalyst. Among the aliphatic compounds chlorinated hydrocarbon waxes are preferred, such as chlorinated paraffin wax, although other reactive aliphatic compounds may be used, by which term "reactive" is meant containing some group such as one or more halogen atoms permitting them to react with an aromatic ring. Such derivatives of petrolatum, fatty acids, fatty alcohols, etc., or other high molecular weight aliphatic compounds may also be used.

The aromatic compound should preferably be a hydrocarbon such as naphthalene, anthracene, diphenyl, or the like, or a phenolic compound such as phenol, the naphthols, anthrols, ketones, etc., or amines such as naphthylamine, aniline, etc. or other aromatic products, such as aromatic esters, ethers, ketones, and the like, as well as methyl, ethyl, and other alkyl derivatives of such aromatic compounds.

It is to be understood that the above-mentioned aromatic hydrocarbons are set forth only as compounds which may be used in the production of the aforementioned synthetic oils and that any aromatic compound containing a replaceable hydrogen which will undergo alkylation under the herein-described process conditions may be used in the production of said synthetic oils.

The condensation of such materials has generally been carried out in the presence of a Friedel-Crafts catalyst such as aluminum chloride, zinc chloride, boron fluoride, etc., preferably in the presence of an inert solvent such as refined kerosene, tetrachloroethane, etc., and at a temperature varying from about room temperature to about 300° F. and generally using proportions of about 2 to 5 mols of the chloro-wax type of constituent to 1 mol of the aromatic constituent. For example, about 10 to 20 parts by weight of chlorinated paraffin wax having about 10 to 20 percent chlorine, preferably about 12 to 15 percent chlorine, in the presence of about 10 to 300 parts, preferably about 25 to 100 parts, by weight of a refined kerosene solvent, and using about 1 to 3 percent by weight of aluminum chloride catalyst based on the weight of the chlorinated paraffin wax can be used.

The reaction is conducted at room temperature for a time period of about 24 hours. Near the end of the reaction period, the temperature is raised to 200° F. until the completion of the reaction. Copious vapors of hydrochloric acid evolve and are allowed to escape from the treating vessel during said reaction. Residual catalyst may be hydrolyzed and removed by washing with water, alcohol, aqueous caustic soda, or dilute hydrochloric acid, etc., settling and drawing off the resultant sludge, and the desired high molecular weight Friedel-Crafts condensation product is recovered from the reaction mass by distillation under reduced pressure such as under vacuum of about 1 to 50 mm. mercury absolute pressure, or by fire and steam distillation to a temperature of about 600° F.

An example of a synthetic oil used in the embodiment of this invention is synthesized in the following manner.

A hard paraffin wax having a melting point of 122 to 125° F. is chlorinated by the direct addition of chlorine in the presence of a trace of iodine and at a temperature of about 200° F. The chlorine is blown through the oil for about 24 hours after which the product is found to contain about 12 percent chlorine which corresponds to a predominate quantity of the monochlor derivative, although there is usually some unchlorinated hydrocarbon. To 90 parts of this chloroparaffin, 10 parts of naphthalene and 10 parts of aluminum chloride are then added with a sufficient quantity of kerosene to completely dissolve the organic materials. The reaction is carried out at room temperature and is found to be substantially complete in about 24 hours, and at this time the temperature is raised gradually to about 200° F.

After the reaction is substantially completed, the product is washed with dilute aqueous caustic soda to hydrolyze and remove the residual catalyst. The viscous sludge is permitted to settle, and the oily Friedel-Crafts condensation product is separated from the reaction mass by vacuum distillation at about 50 mm. mercury absolute pressure. The condensed product has the following inspection:

Gravity	A.P.I.	23.4
Viscosity at 100° F.	SUS	8500
Viscosity at 210° F.	SUS	312
Pour	° F.	65
Flash (COC)	° F.	535
Conradson carbon	percent	1.9
Residual chlorine	do	0.2
Viscosity index		94

The herein-described synthetic oils may be made by the processes outlined further in detail in U.S. Patent Nos. 1,815,022, 2,352,213, 2,410,885, 2,852,557, 2,475,970, 2,882,325, 2,062,354, 2,425,956, 2,353,053, 2,339,493, 2,327,525, 2,251,774, 2,141,593, 2,097,127, and others.

The petroleum paraffin wax which forms a part of the compositions of the present invention is characterized as having a melting point in the range of 125° to 132° F., a penetration at 77° F. in the range of 17 to 23, a viscosity at 210° F. in the range of 36 to 39 SUS and a modulus of rupture at 73° F. of about 270 to 340. Procedures for recovering this specific petroleum paraffin wax from petroleum crude oil are disclosed in U.S. Patents 2,624,501 and 2,906,443.

Generally the improved wet strength corrugated paperboard compositions of the present invention can be prepared by blending together at a temperature in the range of 180° to 250° F. the paraffin wax and synthetic oil until a homogeneous mixture is obtained. The corrugated paperboard is normally immersed in the wax-oil blend at the blending temperature for a period of at least 30 seconds and until the desired amount of wax-oil blend has impregnated the corrugated paperboard.

The corrugated paperboard is withdrawn from the wax-oil blend and permitted to drain and cool to provide a corrugated paperboard composition of enhanced wet stiffness characteristics.

It has been discovered that a thermoplastic composition comprising 0.1 to 1.0 weight percent of the above-described synthetic oil and 99.0 to 99.9 weight percent of the above-described paraffin wax provides corrugated paperboard with a wet stiffness of at least 280 p.s.i. when that corrugated paperboard has been impregnated with 25 to 50 weight percent of the wax-oil composition. The wet strength improvement increases with increasing concentrations of added synthetic oil until the maximum strength imparted to the corrugated paperboard is reached at about 0.5 percent of additive.

As one illustration of the present invention the following examples are presented. The results of preparing compositions as disclosed in these examples are presented in the table under the appropriate example number.

EXAMPLE I

A petroleum paraffin wax prepared in accordance with the procedures disclosed in U.S. Patent No. 2,624,501, having the following characteristics:

Melting point	° F.	129
Penetration at 77° F.		18
Viscosity at 210° F.		39
Modulus of rupture at 73° F.		285
Oil content	percent	0.4

was heated to a temperature of 210° F., and a corrugated board blank was immersed in the molten wax for 30 seconds. The corrugated board was then removed and cooled.

EXAMPLE II

To 99.75 parts of a paraffin wax as described in Example I was blended at 210° F., 0.25 part of a viscous synthetic oil obtained by a Friedel-Crafts condensation of chlorinated paraffin wax having a chlorine content of about 10 to 15 percent with a suitable aromatic compound such as naphthalene, using about 10 to 15 parts by weight of naphthalene to 90 parts by weight of chlornated paraffin wax in the presence of 0.5 to 15.0 percent of anhydrous aluminum chloride (based on the total weight of chlorinated wax) and separating supernatant oil from settled sludge and distilling off low-boiling constituents from said supernatant oil with the resultant residual synthetic oil having the following characteristics:

Gravity	A.P.I.	23.4
Viscosity index		94
Flash (COC)	° F.	535
Pour	° F.	+65
Conradson carbon	wt. percent	1.9
Viscosity at 210° F.	SUS	312

This synthetic oil was prepared by Friedel-Crafts condensation described in U.S. Patent No. 1,815,022 and others.

A corrugated paperboard blank identical to the blank used in Example I was immersed in said wax-synthetic oil mixture for 30 seconds at 210° F. and then removed and cooled.

EXAMPLE III

A homogeneous mixture of 99.5 percent paraffin wax as described in Example I and 0.5 percent synthetic oil described in Example II was blended at 210° F., and a corrugated paperboard blank identical to that used in Example I was immersed in the homogeneous mixture for 30 seconds and removed and cooled.

EXAMPLE IV

A homogeneous mixture of 99.25 percent of paraffin wax as described in Example I and 0.75 percent synthetic oil described in Example II was blended at 210° F., and a corrugated paperboard blank identical to that used in Example I was immersed in said homogeneous mixture for 30 seconds, removed, and cooled.

EXAMPLE V

A homogeneous mixture of 99.15 percent paraffin wax as described in Example I and 0.85 percent synthetic oil as described in Example II was blended at 210° F., and a corrugated paperboard blank identical to that used in Example I was immersed in said homogeneous mixture for 30 seconds, removed, and cooled.

EXAMPLE VI

A homogeneous mixture of 99.0 percent paraffin wax as described in Example I and 1.0 percent synthetic oil as described in Example II was blended at 210° F., and a corrugated paperboard blank identical to that used in Example I was immersed in said homogeneous mixture for 30 seconds, removed, and cooled.

The samples of corrugated paperboard which were treated according to the conditions set forth in Examples

I to VI were all subjected to identical conditions in the following test procedure.

A section of the wax-synthetic oil impregnated corrugated board was subdivided into three 4 inch by 4 inch sections. These sections were immersed in 36° F. water for 2 hours, simulating extremes of high humidity cold storage. After 2 hours the test specimens were removed, and three 1 inch by 4 inch sections with the 4 inch edge perpendicular to the flutes were cut from the inner part of the specimens. The stiffness of these sections was measured parallel to the flutes on both sides using the Tinius-Olsen Stiffness Tester of a 6 inch-pound moment capacity. The force required in pounds per inch squared to give a 3 degree deflection as measured on the stiffness tester was recorded. The average of six measurements was determined and was recorded in the following table. A sample of untreated corrugated board tested under the given conditions was too limp to measure. Stiffness was estimated to be approaching zero.

TABLE I

	Blend comp., percent		Wet stiffness, lb./in.^{2} average	Wt. percent wax blend	Wet stiffness average lb./in.^{2} per percent wax pick-up
	3,425	PDX			
Blank	0	0	(1)	0	0
Example I	100	0	255	39	6.5
Example II	99.75	0.25	330	41	8.0
Example III	99.5	0.50	400	42	10.0
Example IV	99.25	0.75	390	43	9.1
Example V	99.15	0.85	340	41	8.3
Example VI	99.0	1.0	280	38	7.4

[1] Unmeasurable.

The improved wet stiffness characteristics of the corrugated paperboard compositions of the present invention as illustrated by Examples II to VI when compared with untreated corrugated board and corrugated board which contains only wax as shown by the blank and Example I respectively in the table are clearly evident. Also it can be specifically noted that an unusually synergistic effect is achieved in the compositions of the present invention.

This synergism is apparently the result of a maximum resistance to water penetration of the composition in this form, thereby providing a significant improvement in wet stiffness properties.

We claim:

1. An improved corrugated paperboard having a wet stiffness of at least 280 p.s.i. which comprises corrugated paperboard impregnated with 25 to 50 weight percent based on the total weight of the paperboard composition of a thermoplastic composition consisting essentially of

(a) 99.0 to 99.9 of petroleum paraffin wax characterized as having
  (1) a melting point in the range of 125°–132° F.,
  (2) a viscosity at 210° F. in the range of 36–39 SUS,
  (3) a modulus of rupture at 73° F. in the range of 270–340, and

(b) 0.1 to 1.0 weight percent of a synthetic oil obtained by a Friedel-Crafts condensation of a chlorinated paraffin and an aromatic compound, said oil being characterized as having
  (1) an API gravity at 60° F. in the range of 23–26,
  (2) a viscosity index in the range of 90–95,
  (3) a viscosity at 210° F. in the range of 300–315 SUS, and a Cleveland Open Cup flash point in the range of 400–600° F.

2. An improved corrugated paperboard according to claim **1** containing 35 to 45 weight percent of the thermoplastic composition.

References Cited

UNITED STATES PATENTS

2,085,373	6/1937	Loane et al.	106—270
3,023,156	2/1962	Podlipnik	117—158 X
3,033,708	5/1962	McKee	117—158 X
3,139,353	6/1964	Wommelsdorf et al.	117—158 X
3,145,118	8/1964	Mahoney	117—158 X

OTHER REFERENCES

Warth, A.L., The Chemistry and Technology of Waxes, 1956, pp. 798, 780–781, 791–792.

WILLIAM D. MARTIN, Primary Examiner

M. LUSIGNAN, Assistant Examiner

U.S. Cl. X.R.

106—270, 271, 285; 117—154, 168; 161—235