Sept. 17, 1968 C. W. WILKINS 3,402,068

METHOD OF IMPROVING WET STRENGTH PROPERTIES OF PAPERBOARD

Filed Nov. 12, 1964 3 Sheets-Sheet 1

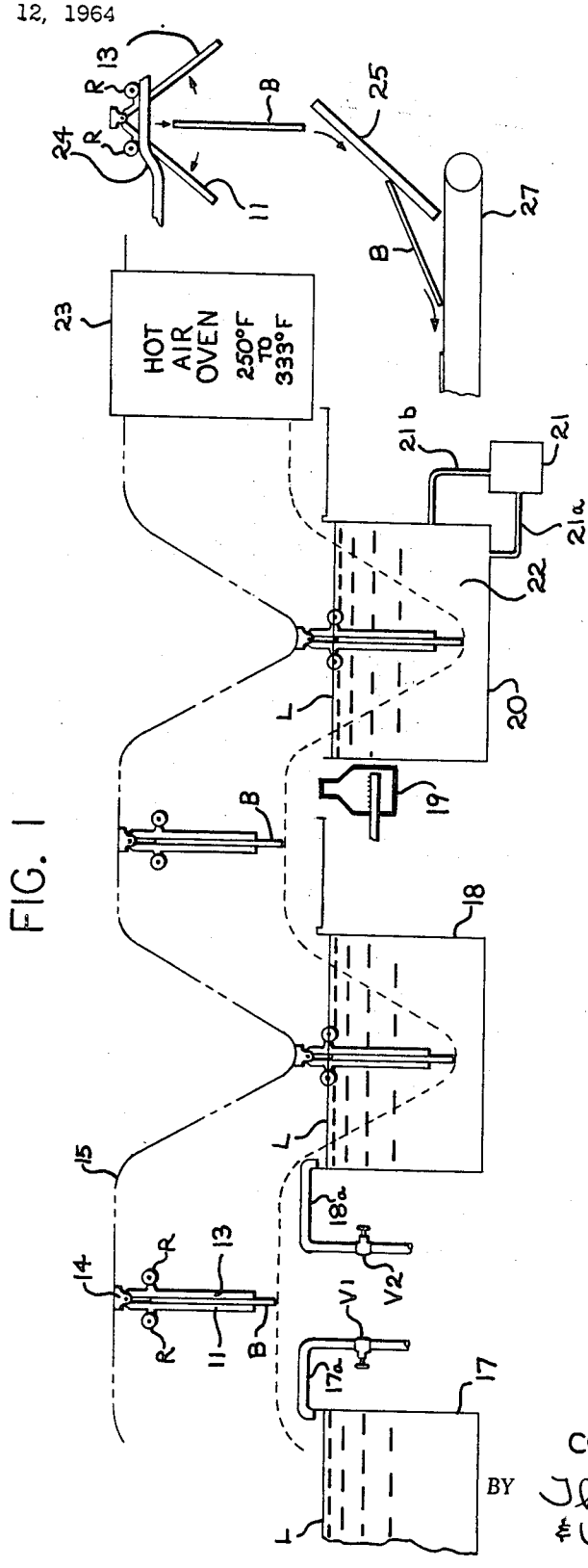


FIG. 1

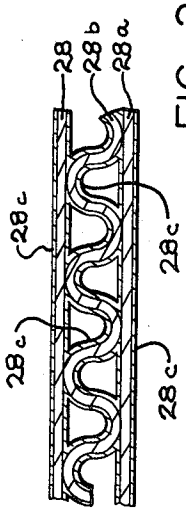


FIG. 2

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METHOD OF IMPROVING WET STRENGTH PROPERTIES OF PAPERBOARD

Filed Nov. 12, 1964 3 Sheets-Sheet 2

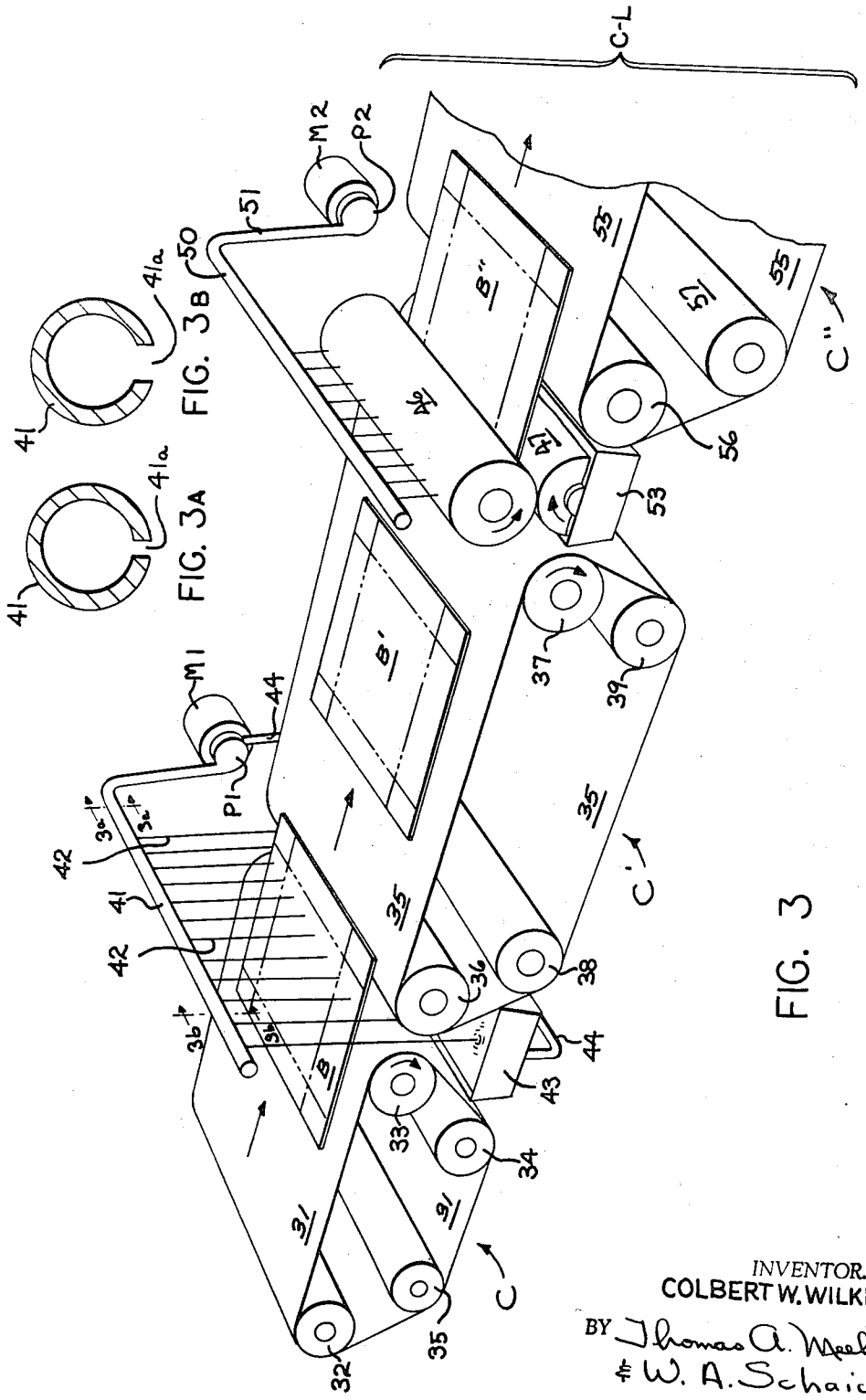


FIG. 3

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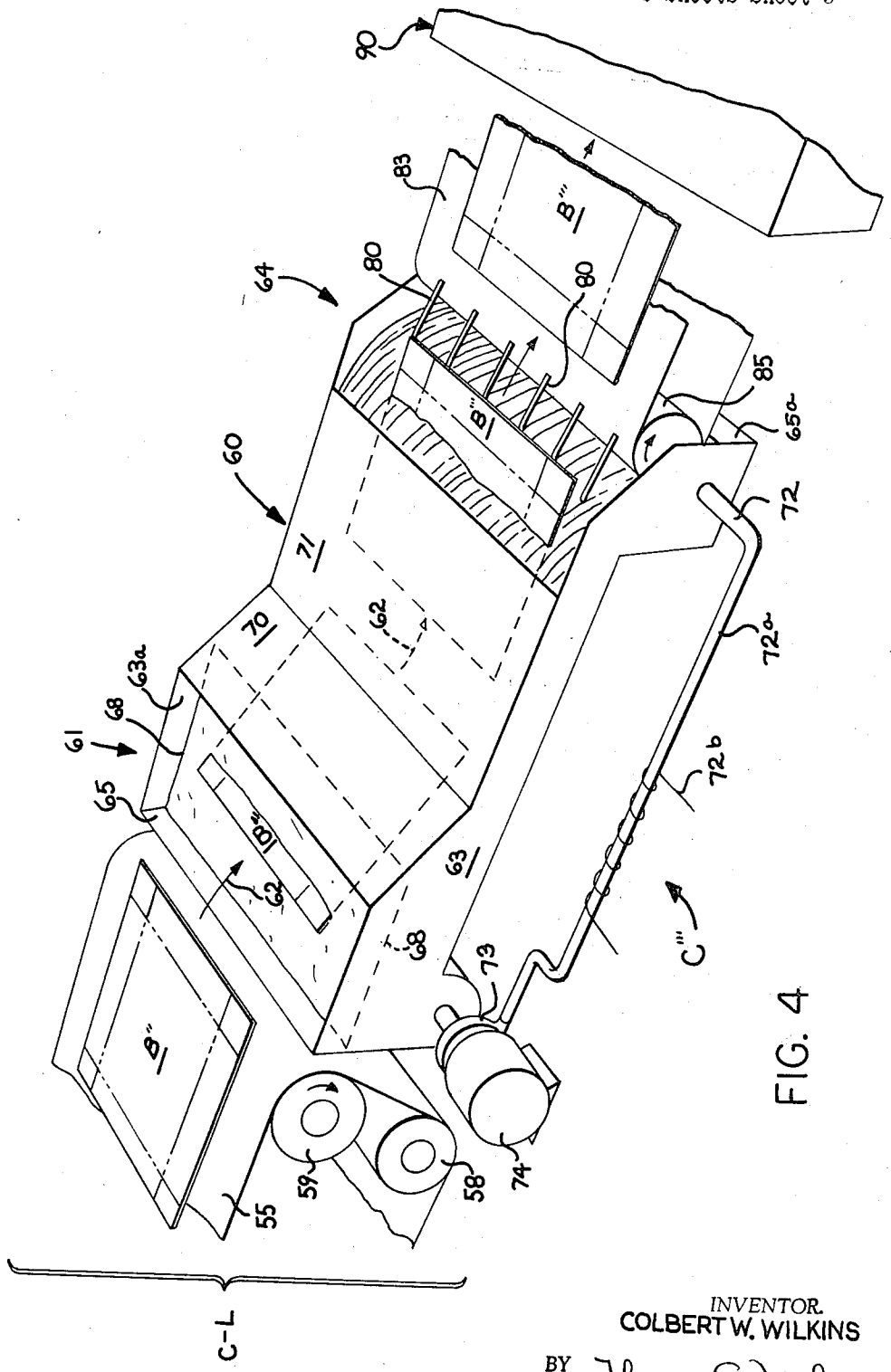


FIG. 4

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United States Patent Office 3,402,068
Patented Sept. 17, 1968

3,402,068

METHOD OF IMPROVING WET STRENGTH PROPERTIES OF PAPERBOARD

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Filed Nov. 12, 1964, Ser. No. 410,508
8 Claims. (Cl. 117—119.8)

ABSTRACT OF THE DISCLOSURE

A method of imparting to corrugated board combined properties of resistance to moisture and inherent strength when wet by the steps of applying to the corrugated board a relatively fluid liquid which includes a partially polymerized resinous substance capable of further polymerization to the thermoset state, immediately immersing the impregnated board into a molten bath of a wax which simultaneously effects further polymerization of the resinous substance and, at the same time, becomes attached to the board surface and thereafter converting the wax-bearing impregnated board to a non-tacky state.

The present invention relates broadly to the art of paper manufacture. More particularly, the present invention relates to a technique for improving the wet strength properties of paperboard, and particularly corrugated board.

Corrugated board is known in the paper art as comprising a pair of facer sheets of paper having secured therebetween, using a suitable adhesive, a convoluted medium sheet of paper; the latter lending strength coupled with lightness. Corrugated board is an ideal material for forming containers, cartons and the like. Corrugated board can be cut, slotted and scored in a variety of designs such that a variety of products can be packaged in containers or cartons formed thereof. In many respects, corrugated board is superior to solid fiberboard. These are principally lightness and resistance to impact and shock.

Both paperboard, broadly, and corrugated board, more specifically, are possessed of an inherent shortcoming encountered in shipping the ultimate package formed thereof. Thus, whether the shipping be by rail, freight, air or truck, moisture is frequently encountered both in the form of standing water, in the form of moisture encountered from the weather, moisture encountered from splashing, moisture inherent in the product, such as foods or vegetables, or moisture present by reason of accidental breakage of the product contained in the carton formed of the paperboard product. A particular use for both fiberboard (sometimes referred to as solid board) and/or corrugated board is in the fabrication of cartons or containers for the shipment of beverages, e.g., soft drinks and beer, through the various distribution levels from the bottler to the consumer and return.

Various treatments have been proposed for purposes of improving the resistance to corrugated board to moisture, wetness, standing water, etc. Unfortunately, none of the proposed treatments have been found to be the complete answer. Generally, it has been found that the present treatments are deficient in that once the preliminary resistance imparted by the treatment is dissipated, the water readily penetrates the fiber sheet material and reduces it to a strengthless soggy mass.

It is accordingly a general object of the present invention to provide a method of treatment of fiberboard and/or corrugated board blanks so as to overcome the problems hereinabove enumerated.

It is also an object of the present invention to provide an improved corrugated board which, by reason of the treatment described herein, enables it to resist moisture and even standing water to a greater degree than heretofore known.

It is additionally an object of the present invention to provide a corrugated board which, by reason of the treatment herein provided, permits it to retain its strength, particularly its resistance to compression, even though exposed to water for extended periods of time.

It is also an object of the present invention to provide a method of treating a corrugated board blank which method of treatment is readily compatible with existing and conventional paper manufacturing techniques.

It is still another object of the present invention to provide a method of treatment as described herein which employs materials which are readily available and are compatible with conventional paper manufacturing operations.

It is also an object of the present invention to provide a treatment and method which can be employed and adapted to conventional operations with a minimum of difficulty and which method employs a time cycle which is economically desirable.

It is likewise another object of the present invention to provide a method of treatment which is extremely flexible in that variations in materials, time and temperature can be employed and/or selected in accordance with the degree of water imperviousness, strength and/or crush strength desired.

The foregoing as well as many other objects of the present invention will become apparent to those skilled in the art from the following detailed description taken in conjunction with the annexed sheets of drawings and the recitation of examples; the sheets of drawings showing, for purposes of illustration only, several embodiments of the present invention.

In the drawings:

FIG. 1 is a schematic side elevation view of an operation or technique for imparting the desirable wet strength properties as described hereinabove to a sheet of corrugated board, usually in the form of a "blank."

FIG. 2 is a sectional view of a piece of corrugated board treated in accordance with the present invention.

FIGS. 3 and 4 are perspective views, partially broken away, which taken together illustrate an alternative method which may be employed to impart unusual wet strength properties to a piece, usually a "blank," of fiberboard, particularly corrugated board.

FIGS. 3A and 3B are respectively sectional views taken on the lines 3A and 3B in FIG. 3.

In accordance with the simplest and most basic embodiment of the present invention, it is proposed that the paperboard, particularly corrugated board, be first brought into impregnating contact with a liquid polymerizable resin component, followed by exposure of the treated board to a controlled liquid bath under conditions conducive to thermal polymerization of the resinous component and final drying of the thusly treated board. In a preferred embodiment, the liquid polymerization bath is composed of a wax which accomplishes simultaneously (a) an in-situ polymerization of the previously applied polymerizable liquid and (b) contemporaneous pick-up of some of the wax lending thereby, in composite, a doubly treated board possessing resistance to moisture and remarkable strength properties even under extremely wet conditions.

Referring now more particularly to the drawings, there is disclosed schematically several alternative embodiments for accomplishing the improved treatment in accordance with the present invention.

In FIG. 1, a "blank" B formed of fiberboard or corrugated board is held in a holder H composed of vertically depending "wicket" or finger elements 11 and 13 con-

nected to a common link **14** traveling on an endless conveyor **15**. The "wickets" or fingers **11** and **13** each bear oppositely projecting rollers R which serve a release function as to the "blank," as described hereinafter. The "blank" B held in the holder H, as shown in FIG. 1, has just emerged from a dip tank **17** containing a liquid constituting a polymerizable resin system, as will be described in more detail hereinafter. An inlet **17***a* controlled by valve V–1 supplies the liquid polymerizable system to tank **17** as needed. The "blank" B thence proceeds to the right and downwardly into a dip tank **18** which likewise contains a polymerizable resin system to the level L, as in the tank **17**. Feed line **18***a* supplies additional liquid resinous component to tank **18** as controlled by valve V-**2**. Emerging from the tank **18**, the "blank" B proceeds beneath a jet heater **19** which serves to remove excess liquid component of the foregoing resinous systems. Proceeding by the heater **19**, the "blank" B proceeds down into dip tank **20** filled with a bath **22** of a liquid held at a temperature conducive to polymerization of the resinous system. Heat exchanger **21** controlled by a pump, not shown, recirculates the bath liquid **22** from the tank **20** via line **21***a* and back to the tank via line **21***b*. The liquid level tank **20** is also designated by the reference numeral L. The "blank" held by the holder H then proceeds upwardly and laterally through a hot air oven **23**. From the hot air oven, the holder H proceeds to the right wherein the rollers R encounter a cam contact **24** which causes the roller elements **11** and **13** to spread apart as pivoted about the element **14**, whereby the "blank" B drops down to an inclined conveyor **25** and thence to a final conveyor **27** which delivers the treated "blanks" to an appropriate stacking or storage operation.

The treated "blank," preferably formed of corrugated board, is shown in partial section in FIG. 2. It is composed of spaced facing or liner sheets **28** and **28***a* having sandwiched therebetween a convoluted corrugated medium **28***b*. The just-mentioned components are impregnated with a polymerizable resinous system, as above and hereinafter described, and also bear a wax coating **28***c* in accordance with a preferred embodiment of the present invention, wherein the wax operates as the liquid polymerization bath for the polymerizable resinous system.

Another operation which may be employed and constitutes a method in accordance with the present invention is schematically illustrated in the perspective views presented by FIGS. 3 and 4, which should be taken together in linear sequence as indicated by the "connect lines" C–L at the right of FIG. 3 and at the left of FIG. 4. In this operation, a plurality of end to end continuous conveyor arrangements are employed. The first conveyor arrangement C is shown at the left of FIG. 3. To the right of conveyor C lies conveyor C′, then conveyor C″ (partly in FIG. 3 and partly in FIG. 4) and, lastly, conveyor C‴ (FIG. 4). The conveyor C is composed of an endless moving belt **31** entrained over upper rollers **32**, **33** and lower rollers **34** and **35**, one of which is a drive roller (not shown). A "blank" B is suitably fed to and lies flat on the upper horizontal course of the belt **31**. The "blank" proceeds to the right, passing to adjacent conveyor C′ composed of an endless belt **35** entrained over a similar set of upper rollers **36**, **37** and lower rollers **38** and **39**. The endless belts **31** and **35**, at their nearest juncture, are separated by a small distance **40**, above which is situated a perforate pipe **41** having a downwardly opening slot **41***a* (FIGS. 3A and 3B) of increasing size in a direction away from the pump P–**1**, traversing the path of the conveyors and the "blank" B. A pump P–**1**, driven by motor M, delivers a supply of liquid polymerizable material to the pipe **41** which delivers it in the form of a "curtain" **42** through the slot **41***a* and thereby descending upon the "blank" B passing therethrough. Excess liquid resin system passes through the space **40** into a catch pan **43**, provided with a drain line **44** which extends back to the suction side of pump P–**1** for recirculation to the "curtain" coater pipe **41**. The "blank" B′ on conveyor C′ is thusly impregnatingly exposed to a liquid polymerizable component. From the conveyor C′, the "blank" passes still in a planar fashion between counter-rotating rollers **46** and **47** arranged in vertical, almost tangetial counter-rotating relationship. Both the rollers **46** and **47** are covered with a layer of felt and are vertically spaced apart just enough to frictionally engage the "blank" and urge it therethrough. Perforate pipe **50** fluidly connecting with vertical stand pipe **51** to pump P–**2**, driven by motor M–**2**, furnishes a supply of a second polymerizable liquid system to the felt surface of roll **46** from which it passes to the upper surface of the "blank." Roll **47**, which is vertically underneath roll **46**, rotates in a pan **53** supplied with the same or a different liquid resinous component. The surface of the roll **47** passes beneath the liquid level within the pan **53** and carries sufficient of the liquid into impregnating contact with the lower surface of the "blank." Emerging from the delivery side of the counter-rotating rolls **46** and **47**, the "blank" B″ passes onto conveyor C″ composed of endless belt **55** entrained around rolls **56**, **57** (FIG. 3) and **58**, **59** (FIG. 4). The thusly treated "blank" B″ passes from the conveyor C″ to the conveyor system C‴ which also functions as a polymerization unit. The conveyor system C‴ is composed essentially of an elongated tank **60** having an upper inlet opening **61**, spaced slightly from the delivery end of the conveyor belt **55** for ready receipt of the "blank" B″, as it proceeds from the belt with forward inertia in the direction indicated by the arrow **62**, and a delivery end **64**. The tank is defined by spaced vertical side walls **63** and **63***a* and spaced vertical end walls **65** at the inlet end and **65***a* at the delivery end. The tank contains a continuously moving stream of molten wax to a level indicated by the line **68**. The inlet end **61** of the tank is vertically deeper than the midway portion **69**. Similarly, the tank proximate the downstream end wall **65***a* is deeper than the midway portion **69**. A top wall segment **70** spaced from end wall **65** proceeds downwardly at an angle to connect with adjoining horizontal wall segment **71**. Segments **70** and **71** connect with upper edges of side walls **63** and **63***a*. The top wall segments **70** and **71** cooperate to direct the passage of the "blank" through the tank **60** and particularly in submerged relationship with the moving wax. The wax leaves the tank **60** at the delivery end **64** via exit line **72** and passes rearwardly through line **72***a* to a pump **73** driven by a motor **74**. The pump keeps the wax circulating through the tank and also in heat exchange contact with heater **72***b* suitably controlled to maintain the molten wax bath at a given temperature.

The resin-treated board "blank" B″ enters the tank **60**, as indicated by the arrow **62**. The inlet portion of the tank **61** is open so that, assisted by gravity, the "blank" proceeds naturally downwardly into the bath of molten wax. The rapid circulation or movement of the molten wax in the tank **60**, proceeding from the inlet **61** to the outlet **64**, carries the board to the right in a submerged relationship with the molten wax by reason of the slanted upper wall **70** and the adjoining wall **71**. The wax polymerized and treated board B‴ emerges from the stream of wax W at the outlet **64** as assisted by spaced fingers **80** which extend horizontally proximate a pick up conveyor belt **83** carried by a pair of spaced rollers, only the leftmost one of which **85** is shown. The wax stream at the outlet end of the tank **60** falls downwardly between the fingers into the deep segment of the tank proximate the end wall **65***a* and is immediately recirculated via line **72** and pump **73** to the inlet end of the tank **61**. The wax-treated board proceeds on the conveyor **83** into a post curing hot air oven **90** for final drying of the wax and resin-treated board as needed,

thereby converting the thus treated board to a tack-free state.

The various conveyor belts disclosed in the drawings may, of course, desirably be perforated or of metal link construction, providing for drainage of excess liquid. Also, appropriate "catch" pans may be employed where needed. Neither of these details are illustrated in the drawings since they would only interfere with clarity.

In the foregoing figures, there have been illustrated several techniques for treating paperboard in order to accomplish the desired result and produce the board of desired properties. Thus, in FIG. 1 it has been shown that the treatment in accordance with the present invention can be accomplished by a dipping technique, utilizing one or more baths containing a polymerizable resinous component. The latter, of course, can be monomeric or a system of copolymerizable substances. It should be appreciated that the resinous treatment with liquid polymerizable materials may be effected in a single bath, rather than in two baths as illustrated. Similarly, in FIG. 3 it has been shown that a resinous treatment can be afforded by use of a curtain coating or essentially a flooding operation as imparted by the curtain coating delivery pipe **41** controlled by pump P–1. Depending upon the choice of the liquid polymerizing systems, the roller coating step shown in FIG. 3 (the rollers being identified by the reference numerals **46** and **47**) may be dispensed with. Conversely, the curtain coating operation employing the curtain coater **41** and pump P–1 may be dispensed with in favor of the felt roller coating operation as shown at the right hand of FIG. 3, utilizing counter-rotating, slightly spaced rollers **46** and **47**.

In common, in accordance with all treatments representing embodiments of the present invention, are a first treatment with a liquid polymerizable resin system which may be a monomeric system or a copolymeric system and a subsequent elevated temperature liquid bath capable of initiating and achieving in-situ polymerization of the monomeric or copolymeric resinous system. Ideally, the in-situ polymerization bath is a molten wax. Examples of resin systems, which may be utilized as impregnating dipping materials in accordance with the present invention, may be mentioned urea aldehyde resins, melamine aldehyde resins, phenol aldehyde resins, modified resins of this type and mixtures of such resins and modified resins. Ideally, the resin should be fairly dilute or fluid as to favor rapid impregnation or transference into the paper component of the paperboard or the corrugated board. An extremely viscous resinous system would not be compatible with the achievement of rapid impregnation. To this end, the resin may be desirably diluted with a solvent or even a monomer copolymerizable with the resinous system.

While the treatment in accordance with the present invention involving a treatment with a resinous system, followed by a wax curing and wax pick-up, achieves a board of increased water imperviousness, such may be accomplished by brittleness, lending relative impracticability as a factor in converting the "blanks" so treated into a container definitive of a shape for the product to be shipped therein. Brittleness, of course, should be avoided and it is an important aspect of the present invention that brittleness is considerably avoided by effecting substantial polymerization in the wax bath which is substantially devoid of oxygen or air. It is thus believed that the presence of air and/or oxygen during polymerization increases the brittleness of the ultimate board. By means of the present invention, air and/or oxidizing conditions are substantially avoided, leading to avoidance of brittleness, but with the maximum of polymerization which goes hand-in-hand with the maximum in resistance to moisture and even standing water.

The invention will now be outlined in more considerable detail by the following recitation of examples constituting various treatments together with the compilation of test data gathered from boards so treated, that is, in accordance with the invention and, as well, control boards; the latter being run for purposes of comparison in order that the desirable attributes and properties imparted by the practice of the present invention may be more clearly demonstrated.

The polymerizable liquid resin systems for impregnating fiberboard, and particularly corrugated board, in accordance with one aspect of the present invention may be prepared by reacting partially copolymerizable monomers, such as melamine, urea, phenol and like formaldehyde polymerizable monomers, with formaldehyde and similar aldehyde group containing monomers. One may also use commercially available partially polymerized and still polymerizable resin systems in the form of solvent solutions or aqueous resin dispersions.

In Table 1, there is listed a number of resin systems which were prepared, representing combinations of polymerizable melamine, urea and phenol formaldehyde resins together with various solvents and other aldehyde monomers. In a series of runs, resin systems were applied several different ways to 7 x 12 inch specimen corrugated boards characterized as 200# test–C Flute.

TABLE 1.—RESIN SYSTEM IN PARTS BY WEIGHT

Resin Number	Type Resin			Diluent				
	MF [a]	UF [b]	PF [c]	Methanol (99%)	Formalin (37%)	Butaraldehyde (98%)	Paraldehyde (98%)	Water
MF 1	80			20	5		20	
MF 2	80			20			20	
MF 3	70			35	10		20	
MF 4	70			35	10	20		
MF 5	100				40	25		
MF 6	70			15	30	15		
MF 7	100			33				
MF 8	100							33
UF 9		200			163			
PF 10			504	58	425			
PF 11			590	216				
UF-PF 12		150	65	164				
UF-PF 13		250	450		100			
14	Polymerizable reaction product of maleic anhydride (MA) and methanol (ROH).							
UF 15		500						

[a] Polymerizable methoxylated melamine formaldehyde resin (80% solids); "Cymel 470" marketed by American Cyanamid Company, St. Louis, Mo.
[b] Polymerizable urea formaldehyde resin (85% solids): "UF-85" marketed by the Nitrogen Division of Allied Chemical & Dye Corporation, New York, N.Y.
[c] Polymerizable phenol formaldehyde resin (46% solids); "AMRES 1430" marketed by Pacific Resins & Chemicals of Newark, Ohio.

The test boards were combined in a conventional corrugator using conventional water resistant adhesives, for example, resorcinol-treated starch adhesives. The adhesive used herein is marketed as "Stabind 5030" by the Staley Manufacturing Company of Decatur, Ill. Upon application of the various resin systems to the specimens of corrugated board in the several runs, usually by dipping for purpose of uniformity, the board was first po-

lymerized by immersion in a primary polymerization bath, most usually a molten wax; the time and temperature being noted. In some runs, the resin-treated and wax-polymerized board was subjected to a subsequent or "post" hot air oven post polymerization. Thereafter, the specimen board of that particular run was tested to determine the amount of resin and wax that had been picked up on the basis of the area of the specimen. Lastly, the specimen boards were subjected to a short column compression test as described in Packaging Engineering, September 1959, page 92, by K. L. Killicut, Forest Products Laboratory, Wis. The short column compression test was run on specimens at 50% relative humidity and after 1 hour and 24 water soaks. The test values were reorded as pounds per inch. The results of the runs are tabulated in Table 2. Listed first in Table 2 is the run number. Secondly is listed the resin system applied, with respect to which reference may be had to Table 1 for the formulation of the the particular resin system. Next, the method of application, e.g., dipping, usually followed by the identity of the primary polymerization bath (together with the time and temperature thereof). Next is listed the "post air" polymerization conditions where utilized. Finally, the solids picked up in pounds per 1,000 square feet for each run is listed together with the result of the short column compression test.

TABLE 2

Run	Resin System	Polymerization		Solids Pick Up MSF, lbs./1,000 ft.[2]	Short Column Compression		
		Primary	Air		50% RH, lbs./in.	Soak	
		Time/° F.	Time/° F.			1 hr., lbs./in.	24 hr., lbs./in.
1	MF (1)	Wax, 1'/250	150'/250	129	263	284	
2	MF (2)	Wax, .33'/230	½'/250	146	334	283	
3	MF (3)	Wax, 3.5'/300		122		432	400
4	MF (4)	Rosin-Wax, 4'/260	180'/250	100	304	302	213
5	MF (5)	Wax, 3'/320		110	401	420	267
6	MF (6)	Woods Metal, 8'/320	2'/320	90.8	296	179	162
7	MF (6)	do	17'/320	90.8	314	221	211
8	None				152	20	
9	MF (6)	Ampro 30 Wax, 8'/320	15'/320	107.9	403	359	182
10	None	do	15'/320	63.3	244	67	
11	MF (6)	None	15'/320	40.1	275	164	132
12	MF (7)	Wax, 10'/320		121	348	223	124
13	MF (8)	Wax, 10'/320		158	329	247	121
14	MF (6)	Wax, 10'/320		108	330	323	195
15	None	Wax, 10'/320		53	217	57	52
16	do				144	14	12
17	UF (9)	Wax, 10'/320		109.6	267	224	155
18	PF (10)	Wax, 10'/329		116.5	296	262	158
19	PF (10)		30'/320	30.9	255	130	124
20	PF (11)	Wax, 10'/329		101.7	400	277	211
21	PF (11)		30'/320	44.9	282	147	136
22	UF and PF (12)	Rosin-Wax, 10'/290	30'/300	122.2	252	216	126
23	UF and PF (13)	Paraffin 2'/240	45'/300	34.9	360		277
24	MA and ROH [1] (14)	Rosin-Wax, 5'/290	30'/300	161.5	186	70	69
25	UF (15)	S.A.E. 20 Oil, 10'/330		97.1	213	178	71

[1]Polymerizable reaction product of maleic anhydride and methanol.

In Run No. 1 the resin system was applied by brush. In Run No. 2 the resin system was poured into the flutes of the corrugating medium. In all other runs where a resin system was utilized, a dipping operation was employed.

For purposes of comparison, Runs 1–5 may be considered together. Run No. 4 demonstrates that a rosin-wax mixture may be utilized as a primary polymerization medium. Run No. 1 demonstrates that the resin system may be brushed onto the surfaces of the corrugated board specimen. Run No. 3 demonstrates satisfactory polymerization can be achieved in as little as 3½ minutes at the elevated temperature of 300° F., even in the absence of a subsequent hot air polymerization or cure.

Runs 6–11 may also be compared. Of these, Runs 8, 10 and 11 are controls. Runs 6 and 7 illustrate the feasibility of Woods metal in place of molten wax. Woods metal, also known as "Woods alloys," are alloys of varying amounts of bismuth, lead, tin, cadmium and indium. Most of the Woods alloys have a composition falling within the range of 35–67% bismuth, 16–40% lead, 8–26% tin, 0–20% cadmium and indium. They may be of eutectic or non-eutectic composition; eutectic compositions being preferable by reason of their lower melting point reaching as low as 117° F., providing thereby a broader spectrum of molten bath temperatures available with the "Woods alloy" type of liquid polymerization bath. A specific "Woods alloy" having a melting temperature of 117° F. is composed of 44.7% bismuth, 22.6% lead, 8.3% tin, 5.3% cadium and 19.1% indium. Run No. 9 illustrates a resin treatment and wax polymerization and pick up which result in a board having exceedingly high wet strength properties. Comparison of this run with Runs 10 and 11 reveals the unexpectedly high strength values achieved. Run 10, of course, as indicated, represents a corrugated board which had only been dipped in a wax bath, whereas Run 11 typifies a board having only the resin dipped treatment but not the wax polymerization.

Runs 12–14 provide for a basis of comparison taken with Runs 15 and 16 which are controls. Run No. 14 demonstrates the achievement of extremely high strength results even though wet.

Runs 17–25 illustrate the use of other polymerizable resin systems, such as urea formaldehyde and phenol formaldehyde and, as well, a reaction product of maleic anhydride and methyl alcohol. Run No. 23 demonstrates the utilization of paraffin as a polymerization bath. Run No. 25 illustrates the use of S.A.E.–20 oil as a polymerization bath. Runs 18 and 19 offer a basis of comparison, since in Run 19 air was utilized as a polymerization medium rather than wax, resulting in lower compression values. A similar comparison is offered by Runs 20 and 21 wherein the air polymerized resin system of Run 21 is inferior in wet compression properties to that of Run 20.

It is believed that the foregoing runs (as tabulated in Table 2) demonstrate the usability of heat polymerizable polymeric systems. In the same manner as described hereinabove, the copolymer system composed of dihydric alcohols and poly-carboxylic acids represents a useful polymerizable resin system of utility in the practice of the present invention.

Another resin system constitutes the epoxy system as, for example, obtained by partially reacting bisphenol A and epichlorohydrin. Still another suitable polymeric system is represented by the various prepolymers formed from the diamines and various di-isocyanates. Abietic acid complexes as, for example, result from the reaction of abietic acid and tri mellitic anhydride represent another system within the purview of the invention. Additionally, turpentine may be employed as a first treatment followed

by immersion in molten wax containing dibutyl phthlate in accordance with the present invention.

In every case the polymeric system, whether applied as one or two treatments, should be applied as fairly fluid liquids. Preferably, the viscosity should not exceed about 150 centipoises since the impregnation of the fiberboard, whether by dipping, roller coating or the like, proceeds more satisfactorily. Resin systems which are inherently viscous or which as obtained on the market are too viscous can be diluted, particularly with a compatible non-aqueous monomer or a compatible solvent. The following is a listing monomeric reactants which are copolymerizable with one or more of the resin systems mentioned so far herein: formalin, fufural, glyoxaldehyde, glutaraldehyde, furfuraldehyde, butyraldehyde, paraldehyde, paraformaldehyde, benzaldehyde, salicylaldehyde, acrolein, aldol (hydroxy butyraldehyde), methanol, hexamethylene tetramine, menthane diamine, glacial methacrylic acid, phthalic anhydride, maleic anhydride, tri mellitic anhydride, ethylene glycol, polyglycol, etc. A viscosity close to that of water is eminently satisfactory for the polymerizable resin systems contemplated.

While a wax bath represents a preferred substance for effecting polymerization of the monomeric or polymeric system, a heated finely divided solid "shot" may in certain cases be introduced through the parallel spaced passageways defined by the convoluted corrugating medium in combination with the facing of liner sheets. Thus, this expedient may be employed in order to effect polymerization but with a minimum of air or oxidizing conditions as alluded to hereinbefore.

Having in mind the overall achievement of wet compression strength properties of the ultimately treated corrugated board, it is most preferred that the resinous treatment be selected from the thermosetting liquid polymerizable resins including the melamine aldehyde resins, the urea formaldehyde resins and the phenol formaldehyde resins. These resins are also preferred by reason of the relative ease of impregnation and processability and favorable cure rates, particularly upon immersion in molten wax maintained at a temperature in the neighborhood of 300° F. Particularly efficacious results are obtained where the resin system includes components, either solvent or monomeric, which tend to reduce the viscosity of the resin system or, stated in another way, increase its fluidity leading to a greater degree of impregnation. Additionally the invention contemplates the desirable feature wherein one or more of the components is monomeric and polymerizable with the basic resin system involved. Note, for example, Resin No. MF 6 (see Tables 1 and 2) which includes a melamine formaldehyde polmerizate as the basic system, but includes additionally a proportion of methanol, a proportion of formalin and a proportion of butaraldehyde. The latter material is essentially 98% aldehyde as is acetaldehyde and trioxane. Paraformaldehyde is available in a 98% purity form and also in 91% purity flake. These latter materials and equivalent high purity aldehydes are most desirably included as constituents in the water soluble, partial polymerizates of systems; urea formaldehyde, melamine formaldehyde and phenol formaldehyde. The amount of these high purity aldehydes to be included in order to improve the compression strength ranges from about 10 to 30 parts per 100 parts of the partial polymerizate, be it a urea, melamine or phenol aldehyde system.

The treatment of the corrugated board specimen in the form of a rectangular blank, which most advantageously has been prescored, may, as indicated hereinabove, be accomplished in a variety of ways. Thus, it may be dipped, it may be "curtain" coated, roller coated, etc. We have found that in any of these a resin pick-up in the range of 15–50% based on total board weight on an oven dry basis can be accomplished and represents a particularly desirable range in terms of improvement. Too much resin pick-up is undesirable since brittleness results whereby folding of the "blank" leads to cracking. Additionally, amounts in excess of 50% lead to a final board which exudes excess resin leading to a matted surface, a condition which is undesirable. Combinations of the foregoing application techniques can be employed where it is desired to employ a two-step application of copolymerizable monomers or a first application of an appropriate monomer, followed by a second treatment with a catalyst or initiator of polymerization for that monomer. Examples include peroxides (benzoyl peroxide) organo metals (cobalt napthenate), dimethyldiammonoium acetate hydroperoxide or azonitrite. In any of these, of course, it is contemplated that resin application would be followed in rapid succession by an immersion in molten wax. Corrugated board has also been coated with a concentrated solution of formaldehyde using felt covered rolls followed by a dipping in hexamethylo melamine and lastly, the coated structrue slowly immersed in 185° F. molten wax for a period of 20 seconds. The resultant board, upon examination, revealed that the resin had polymerized and, additionally, wax had been picked up, yielding an extremely water resistant structure.

A particular achievement in accordance with the present invention is the accomplishment of an in-situ polymerization of the resin system in the absence of air, whereby substantial polymerization of the resin system is accomplished without the accompanying brittleness normally associated with polymerization in a hot air oven. Brittleness, as such, is to be avoided since such interferes with the foldability of the relatively foldable components of the blank into carton or container configuration.

Modifications may be resorted to without departing from the spirit and scope of the present invention. Changes in formulations and process conditions obviously suggested by the foregoing are accordingly to be considered included unless violative of the scope of the appended claims.

I claim:

1. The method of imparting to corrugated board resistance to moisture and inherent strength when wet, said method comprising the steps of:

applying to said corrugated board a relatively fluid liquid including a partially polymerized resinous substance capable of further polymerization to the thermoset state, said application effecting penetration of said substance into said corrugated board components,

immediately immersing said corrugated board in a molten bath of a wax substance which is substantially inert to said resinous substance, said wax being at a temperature adapted to thermally advance the further polymerization of said resinous substance, an amount of said wax being picked up by said resin impregnated board to form a coating thereon and

converting sid wax coated and impregnated board to a non-tacky state.

2. The method as claimed in claim 1, wherein said molten wax bath temperature is from about 250° F. to about 330° F.

3. The method as claimed in claim 1, wherein said resinous substance is a liquid, polymerizable thermosetting resin.

4. The method as claimed in claim 3, wherein said resinous substance additionally includes a monomeric aldehyde of a purity of at least 90%.

5. The method as claimed in claim 3, wherein the fluid liquid resinous substance includes a viscosity reducing substance.

6. The method as claimed in claim 5, wherein the viscosity of said fluid liquid does not exceed about 150 centipoises.

7. The method as claimed in claim 4, wherein said aldehydes range from about 10 to about 30 parts per hundred parts of the partial polymerizate.

8. The method as claimed in claim 3, wherein the amount of resin pickup ranges from about 15 to about 50 percent based on total board weight on an oven dry basis.

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