Oct. 19, 1943. B. U. WRIGHT ET AL 2,331,951

PRINTING OF MOLTEN SULPHUR

Filed July 26, 1940

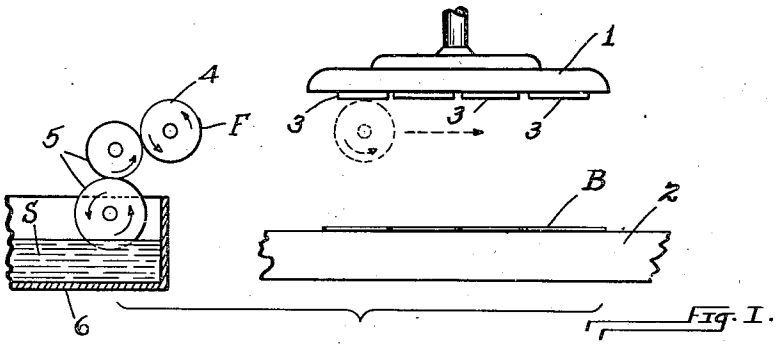


Fig. I.

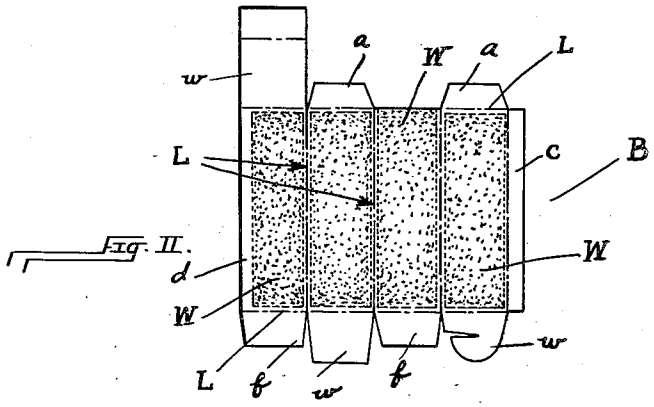


Fig. II.

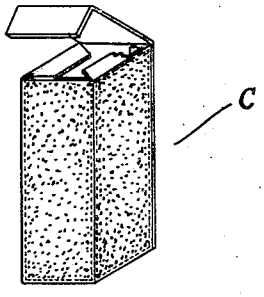


Fig. III.

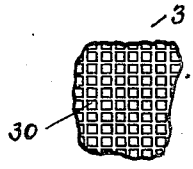


Fig. IV.

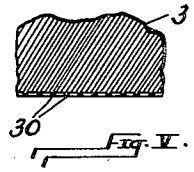


Fig. V.

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Patented Oct. 19, 1943 2,331,951

UNITED STATES PATENT OFFICE

2,331,951

PRINTING OF MOLTEN SULPHUR

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Application July 26, 1940, Serial No. 347,774

2 Claims. (Cl. 117—15)

Our invention relates to paper, fibre-board, cloth and webs of other fibrous material, and consists in improvements in method of and apparatus for treating such webs with sulphur, to the end that the webs shall be strengthened, rendered repellent to moisture, and provided with a hard and smooth surface finish.

Years ago it was recognized that the impregnation of a web of paper or fibre-board with sulphur increased the strength of the web, with the effect that for particular uses the webs might be of lighter and more economical weight than they otherwise might be. It has been known that the sulphur impregnant hardens and toughens the paper, provides a high surface finish, and renders the paper repellent to moisture.

Sulphur is superior to many known impregnants, in that it has a relatively high melting point. It is also peculiarly valuable, in that it is inert; it inhibits fungus growths, and resists the attacks of bacteria and insects.

So far as known, only two methods of producing sulphur-impregnated paper have hitherto been known and used.

In accordance with one of these prior methods the surfaces of the web are coated or dusted with powdered sulphur, and the coated web is heated to a temperature above the melting point of sulphur. Under the influence of heat the applied sulphur coating melts and is absorbed into the body of the web. In elaboration of this method, the powdered sulphur may be mixed in a liquid vehicle, to the end that the sulphur may be more readily and more uniformly applied to and distributed upon the web. Needless to say, the liquid vehicle must be evaporated and driven off before the applied heat can melt the sulphur, to admit of its absorption into the substance of the web.

In accordance with the other known method, the web of paper is immersed in a bath of molten sulphur. It absorbs the sulphur; and upon removal from the bath the saturated web is passed beneath a pressure roll, and the excess sulphur is pressed out and removed.

As distinguished from these prior-art procedures, the procedure of the present invention consists in printing molten sulphur upon the surface of the web. More particularly, a film of molten sulphur is applied to the face of a heated printing instrumentality, typically a printing block, and then such film, while still in fluid state, is transferred from the block to the surface of the web. The film of molten sulphur, so applied under pressure to the surface of the web, is to an adequate degree absorbed into the substance of the web. Upon separation of the heated block from the web, the sulphur impregnant cools and solidifies.

The advantages of the present method, as distinguished from the methods hitherto practised, are that the product is more uniform, and the surface of the web is smoother and harder. The degree of impregnation—the depth of penetration of the sulphur into the substance of the web may be regulated and controlled with precision; the thickness of the sulphur film printed on the web may be varied and regulated, with the consequence and effect that the penetration of the impregnant in the body of the web may be established at a value most effective for the particular use to which the web is to be put. Again, the degree of penetration and the concentration of the sulphur in the body of the paper may be controlled by regulating the temperatures of the molten sulphur and of the printing instrumentality, the thickness of the printing film of sulphur upon the surface of the printing instrumentality, and the presence and the time interval of application of the printing instrumentality upon the paper. Also, as presently will appear, the use of introfiers with the molten sulphur is advantageous, and the degree of modification by the introfier, and the specific material of which the printing instrumentality is formed, and the surface condition of the printing instrumentality are variable factors that are important to ends in view.

From what has been said, it will be understood that in the product of this method the impregnant is of maximum density or concentration at the surface of the web, where the beneficial effects are most needed. The applied sulphur may be caused, and commonly is caused, to form upon the surface to which it is applied a continuous, hard and smooth skin or coating. From the surface of the web inward the density or concentration of the impregnant decreases gradually, and may terminate at some plane intermediate the opposite faces of the web. In such way, not only may the surface hardness of the finished article be properly determined, but the elasticity and flexibility of the web body may be established at the desired value.

The sulphur-impregnated web will accept printers' ink, and thus can be lettered or decorated as can unsulphurized webs of paper.

It is additionally characteristic of the method of this invention that the web may be readily surfaced and impregnated in selected areas of its extent, to the exclusion of other and intervening areas, and this feature is (as known in the art) valuable in the treating of paper-board that is to be used in the construction of cartons, boxes, and other articles formed of folded paperboard blanks. More particularly, it has been found advantageous, in the preparation of paperboard blanks for cartons, etc., to leave the blanks untreated over the areas that receive the usual

adhesive for securing and sealing the cartons in erected condition. Also the blanks are, advantageously, left untreated over narrow areas along the extent of the crease-lines on which the blanks are to be bent and folded in the erection of the cartons, for in this way the folding of the blanks and the erection of the cartons may be effected more readily. The tendency to crack along the crease-lines—a difficulty that is always encountered in a blank that is impregnated with sulphur over its entire area—is not present. Additionally, it will be understood that the blanks may be treated on one side only, with the effect that there shall be no sulphur on the inner surfaces of the erected cartons.

From what has been said, it will be realized that the invention is particularly (though not exclusively) adapted for the preparation of carton blanks, and in such association it will be described.

In the accompanying drawing Fig. I is a fragmentary view, showing diagrammatically in side elevation, and partly in vertical section, apparatus in which the method of the invention may be practised. Fig. II is a view in plan of a carton blank that has been dealt with in accordance with the invention. Fig. III is a view in perspective of the carton erected from such blank. Figs. IV and V are fragmentary views, severally illustrating in plan and in vertical section a refinement in the structure of the printing block embodied in such apparatus.

Referring to the drawing, the reference character B indicates a carton blank—a flat web of paper board, cut and creased in usual way for the construction of a carton C. The web includes four portions W that form the side walls of the carton, portions *w* that provide the top and bottom walls of the carton, flaps *a* and *b* that reinforce the top and bottom walls of the carton, and a flap *c* that in the erection of the carton is glued or otherwise secured to the left-hand edge of the blank (Fig. II), to complete the circumferential continuity of the carton side walls. The blank is impregnated with sulphur over the areas indicated by the dotted shading in Figs. II and III. Along the crease-lines L that define the panels of the finished carton, over the margin at areas *c* and *d* that are to be cemented or otherwise secured in overlapped position, and over the top and bottom flaps *a*, *b*, *w*, the surface of the blank is left untreated with the sulphur impregnant. The blank B may readily be bent and folded on the crease-lines, without risk of cracking of the body of the web, as it is more likely to do if it be impregnated in continuity across those crease-lines; and the union over the areas *c* and *d* may more readily and more effectively be secured, as by glue or cement. It is to be noted that the crease lines L may be formed in the blank before the printing on of the sulphur. Alternately, the crease-lines may be formed during the printing operation, or at any suitable time thereafter.

The carton blank described may after impregnation be coated with paraffin over both the printed and unprinted areas, or the erected carton may be so coated. The paraffin provides additional strength and protection for the impregnated areas of the blank, and renders the unimpregnated areas moisture-proof. Indeed, the paraffin may impregnate the web to the extent that it remains porous and unfilled with sulphur. Paraffin preparations are known that when so applied will not crack along the bends.

Having described a new and useful product of the method of impregnating webs of paper and paper-board, the method per se will be considered. Referring to Fig. I, the exemplary apparatus for the practice of the method consists in a head **1** reciprocable relatively to a platen **2**. The head carries a printing block or a type **3** that, when "inked" with a film of molten sulphur, prints the film upon a paper blank positioned on the platen, over areas defined by the block or type. In this case the web under treatment is a carton blank B, and the printing block or type carried by the head consists, specifically, in a plurality of blocks **3**, that may be understood to be shaped and arranged in plan in correspondence to the shaded areas of the blank of Fig. II. The head **1** is heated (say by steam or by electrical resistors), and the blocks **3** are brought to and maintained at a temperature approximating the melting point of sulphur. When a film of molten sulphur has been applied to the faces of the printing blocks **3**, the head **1** is driven downward, bringing the printing blocks to position upon the surface of the paper-board web B. The film of sulphur is printed upon the web, and molten sulphur enters the substance of the web. When the heated head has remained in contact with the work for a sufficient interval, it is elevated, and the sulphur impregnant cools and solidifies upon and in the body of the web. (In a typical case, employing a web of relatively dense paper-board, the platen **2** was maintained at a temperature of 318° F.; the pressure of application was 85 pounds per square inch of area of the printing blocks **3**; and the interval of contact of the printing blocks with the paper-board was 30 seconds.)

Alternately, the printing blocks **3** may be carried upon a printing roller with the faces of the blocks curved to concentricity with the axis of the roller. In such case blanks B will be advanced beneath the roller, as sheets of paper to be printed are advanced through a cylinder printing press, and the sulphur will be printed upon the blanks over the areas described.

The instrumentalities for applying molten sulphur to the faces of the printing blocks may be such as are convenient. By way of example, a tank **6** is provided, in which a bath S of sulphur is maintained in molten condition. A pair of transfer rollers **5** is arranged to carry molten sulphur upward from the bath, and to apply it in the form of a film F upon the surface of an "inking" roller **4**. Upon receiving an adequate film of molten sulphur, the roller **4** is rolled across the printing blocks **3**, as indicated in dotted lines and by the arrow, and the film is transferred to the printing faces of the blocks.

As mentioned above, the use of an introfier with the molten sulphur is advantageous to the operation, and affords fullest measure of success, and it has also been found that the composition of the printing blocks **3** is important. A properly chosen introfier will facilitate and accelerate the penetration of the sulphur film into the substance of the web that is being impregnated. Additionally, the introfier assists in gaining the desired uniform distribution and adherence of the applied molten film upon the faces of the printing blocks; that is to say, the introfier assists the molten sulphur in wetting the surfaces of the blocks.

The introfier may consist in a member of one or another of the following three groups of solutes, it being noted that the members of each group may be characterized as including in

molecular structure at least two rings of the general benzene type:

Group I

Diphenyl	Dibenzyl
Chlorinated diphenyls	Dibenzyl ketone
Halogenated diphenyls	Fluorene
Diphenyl methane	Carbazole
Phenyl ether	Phenanthrene
Benzyl ether	

Group II

Triphenyl methane	Triphenyl quanidine
Triphenyl chlormethane	Triphenyl phosphate
	Tricresyl phosphate

Group III

Naphthalene	Quinoline
Dinaphthyls	Acenaphthene
Chloro-naphthalenes	Hydronaphthalene
Naphthols	Anthracene
Chlorinated dinaphthyls	

The thickness of the film applied to the printing blocks may be controlled by regulating the clearances between the surfaces of the rolls 4 and 5, and by adjusting the speed of rotation of such rolls, and the speed of traverse of the "inking" roll 4 across the faces of the printing blocks. Regulation of the viscosity of the molten sulphur in the bath also affords control over film thickness The viscosity of the molten sulphur is dependent upon two factors: the temperature of the bath above the melting point of sulphur, and the concentration of the introfier in the molten sulphur. Both of these factors are minutely variable, and it will be perceived, therefore, that the thickness of the film applied to the printing blocks may be nicely regulated, with the effect that the concentration and the depth of penetration of the sulphur into the impregnated paper board may be accurately controlled. The introfier neither interferes with nor impedes the subsequent solidification of the sulphur impregnant.

As already mentioned, the composition of the bodies of the printing blocks is important. Essentially, the blocks must be of material substantially inert to sulphur. Also the material of which the blocks are formed must be susceptible to receiving and retaining an uniformly distributed film of molten sulphur: the blocks must be of such material and surface condition that they have a physical affinity for (that is, they can be wetted by) the molten sulphur, and yet will in the printing release the sulphur film cleanly to the surface of the paper web. Brass provides an excellent material of which to form the blocks. It appears that ordinary cast-iron and steel may be used; so may nickel, and alloys of nickel and copper; aluminum and copper; and other copper alloys.

It remains to be noted that the thickness of the molten film that may be applied to the printing faces of the blocks depends, aside from the factors considered above, upon the nature of the surface of the printing block. If the printing faces of the blocks be smooth, the film of molten sulphur can not be as heavy as if the faces be rough. As a matter of fact, in order to practise the method with the heaviest films that may be desired, the faces of the printing blocks are intentionally roughened, as by serrations machined therein, or by a grid structure 30 given to the faces of the blocks, as illustrated in plan in Fig. IV and in section in Fig. V. Best results in the printing of carton stock have been obtained with brass printing blocks whose printing surfaces have been sanded.

It is contemplated that in the practice of the invention ordinary crude sulphur in molten condition (preferably with an introfier added) will be the impregnating material—the "ink"—which is printed upon and absorbed into the webs of paper, fibre-board, cloth, or other fibrous material, to be treated. In some cases, the sulphur may be combined with other ingredients. Similarly as sulphur, with or without an introfier, compounds and derivatives of sulphur, that owe their effective properties to the presence of sulphur and that possess in large measure similar chemical and physical properties, may be employed. Specifically, compositions such as sulphurized petroleum resin, sulphur-turpentine reaction product, sulphur plasticized with Thiokol, sulphur chloride phenol resin may be used.

The molten sulphur may be compounded with pigments, to afford desired color effects in the product. The molten sulphur may be used as a quick-setting ink, with which letters or designs may be applied in relief on the receiving surface. Watermarks on paper may be simulated, and trade-marks applied. And the sulphur "ink" may be used in marking wearing apparel and other such things as are repeatedly laundered or cleaned.

As exemplary of still another instance in which the invention finds utility, we cite the manufacture of corrugated board, board consisting of two smooth webs of paper glued or cemented upon opposite sides of a corrugated web of paper. In the production of such board each of the two smooth webs may be printed with sulphur on one side, and then assembled upon the corrugated web, with the unprinted surfaces of the smooth webs cemented to the crests of the undulations in the corrugated web. In such way both of the outer, exposed surfaces of the ultimate board are provided with the advantageous printed sulphur finish, while those surfaces of the three webs that lie within the assembly, having no sulphur printed thereon, remain in condition best to receive the cement and to establish and hold the desired bond between the webs.

In the ensuing claims, we use the term sulphurous material to include the material herein specified in its various forms and conditions; namely, sulphur itself, sulphur mingled with an introfier, compounds and derivatives of sulphur that are inert and have also such physical characteristics as to render them amenable to the procedure specified.

We claim as our invention:

1. The method herein described of sulphur-surfacing paper which consists in bringing sulphur to molten state, spreading it upon the surface of a printing block and impressing the outspread film with penetration into the fibre of the paper upon the surface of the paper.

2. The method herein described of producing upon a web of fibrous material an adherent, dense, and inert coating, which consists in spreading upon the surface of a printing block a film of normally solid sulphurous material rendered molten by heat, and impressing the outspread film with penetration into the fibre of the material upon the surface of the web while the web is rigidly supported from beneath.

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