

1

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METHOD OF PREPARING SECURITY PAPER CONTAINING AN ULTRAVIOLET INHIBITOR

Bruce D. Skofronick, Appleton, Wis., assignor, by mesne assignments, to Customark Corporation, Appleton, Wis., a corporation of Wisconsin

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2 Claims

ABSTRACT OF THE DISCLOSURE

A paper product with a security impression and the method of preparation therefor. A selected area of the paper is treated with a liquid composition having an inhibitor chemical comprising an ultraviolet absorbing organic chemical in an amount so that the treated area is invisible in the dry state and visually detectable after wetting the paper.

This invention relates to a paper product with an incorporated security impression, and to a method of making such a paper product.

There have been many attempts and many proposed ways in the art to check the authenticity of various paper, official or otherwise. A particular effort has been concerned with applying impressions which are normally invisible, but which are rendered visible by appropriate manipulative steps. Such an approach has many advantages because it can be applied to many different types of papers, irrespective of the number of conventionally printed visible ink or other impressions applied to the paper. Various types of paper products are desirably adapted for such a security impression mark, such as passports, bonds, official government or private stationery, industrial or artistic drawings, and any type of paper having some meaningful or commercially important visible impression on the surface thereof.

It is a primary object of the present invention to provide a paper product and a method by which a security impression is simply and conveniently applied to paper so that it is invisible in the dry state, and may be rendered visible for checking authenticity or otherwise by the quick, economical and simple provision of wetting the paper.

Another object is a security paper product and method whereby any selected security impression can be applied to any portion of a hard, finished paper surface, and be retained therein to check the authenticity of the paper one or more times.

Another object is the security paper product and method by which the security impression is conveniently and quickly applied to the surface of finished paper in a liquid state, and said paper is put into use after the security impression is converted into a dry state, without visible perception by uninformed handlers; yet is quickly rendered visible for checking purposes by simply wetting the portion of the paper having the security impression.

Another object is the security paper product and method which permits the paper product to be checked for authenticity or the like on repeated occasions because the security impression is retained over an extended period of time, and is capable of undergoing repeated manipulative steps which render the mark visible for security purposes.

Another purpose is a paper product and method on which a security mark can be applied with any selected

2

configuration or design to identify the paper product, to code the paper product, or otherwise provide a meaningful indication, said mark being normally invisible but capable of being rendered visible quickly, simply and cheaply.

Another object is a method whereby few manipulative steps and materials are employed to make a finished paper product with the security mark of such a type that the security mark can be checked for authenticity or other information relative to the paper product.

Such objects are realized, as well as other objects which will become apparent by considering the following disclosure, which teaches representative ways of preparing and using security paper products.

The invention provides that a security impression mark is normally invisible on a surface sheet of paper or in the matrix of the paper but is rendered visible by a very quick and economical manipulation which can be instantly and universally practiced, namely, wetting the paper with water. In the wet state, the previously invisible security mark is rendered visible, and again becomes invisible in the dry state. It is a marked advantage of the invention that such security marks can be repeatedly made visible over extended periods of time by rewetting the paper. There is a further advantage that such security impression mark is ink receptive, by which is meant that it receives printed or other ink impressions without blurring, feathering, skipping or the like. In other words, the security impression can receive normally visible written, drawn or printed impressions. Such visible impressions include the non-ink type, such as pencil, crayola and the like.

The security impression mark or configuration or design is laid down or applied to a portion of the surface of finished paper. The security impression mark is laid down from a liquid composition which contains one or more ultraviolet absorbent organic chemicals and an organic solvent which is removed after application by evaporation, heat or the like. In a sense, the security impression may be said to be printed where a stamp, die or the like is used to impart the design or configuration onto the hard finished surface. The liquid composition may be spread as a film on such impression transferring means and applied with momentary pressure. It will be appreciated, however, that other means may be used for applying the security impression to the surface of the paper, such as manual inscription with a brush or the like. It will be seen that in certain operations a simple hand stamp may be used to put the invisible security impression or mark on occasional papers which are presented to certain agencies such as those which handle secret reports, passports or the like. It will likewise be seen that such security impressions could be continuously impressed on papers in large scale operations by employing a printing roll or printing plate or a stencil operation, or similar means for large scale operations.

The ultraviolet absorbing organic chemicals which are useful in the invention are generally known in the art and represent various benzophenone types, particularly hydroxy and alkoxy types of substituted benzophenones, among which are 2-hydroxy-4-methoxybenzophenone supplied as Uvinul M-40; ethyl-2-cyano-3,2 diphenyl acrylate supplied as Uvinul N-35; 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid supplied as Uvinul MS-40; and 2,4-dihydroxybenzophenone supplied as Uvinul 400. All of the foregoing Uvinul ultraviolet absorbent organic chemicals are made and sold by Antara Chemical Company. Other available and useful ultraviolet absorbing organic chemicals are the series supplied under the design-

nation of Eastman Inhibitors by the Eastman Chemical Company. They are:

HPT—Hexamethylphosphoric triamide
 DHPB—2,4-dihydroxybenzophenone
 OPS—p-Octylphenyl salicylate
 RMB—Resorcinol monobenzoate
 DOBP—4-dodecyloxy-2-hydroxybenzophenone

Other ultraviolet absorbing chemicals commercially available on the market are:

Cyasorb UV9—2, Hydroxy-4-methoxybenzophenone
 Agent AT-539 (Univul N 539)—2 ethyl hexyl-2-cyano-3,3 diphenyl acrylate.

The Eastman inhibitor HPT is supplied as a liquid containing organic solvent, and may be applied in such a form directly to the surface of the finished paper and dried. The OPS and RMB have ester linkages but are believed to convert to hydroxybenzophenones under the influence of ultraviolet rays. Other ultraviolet absorbent chemicals are provided in dry powder form and are converted to a liquid composition by dissolving the powder in an organic solvent. The concentration of the ultraviolet organic chemical absorbing agent in the organic solvent can be varied within selected ranges, depending on the consistency of the composition which the practitioner desires to handle, and the manner of applying the liquid composition to the surface paper. It will be appreciated that the concentration should not be too great because then the workability of the liquid composition is impaired; likewise, it may become more difficult for the ultraviolet absorbing chemical to adhere to the finished paper. On the other hand, the concentration should be present in sufficient amounts so that a visually detectable mark appears after wetting the paper. Understandably, if the concentration is too low, an unsatisfactory type of mark may be laid down in that it has gaps or breaks or streaks in the particular design selected. Such workable concentration can be readily determined without difficulty by those skilled in the art. In general,

a 10% concentration of the organic chemical and organic solvent will provide an operable liquid composition which leads to satisfactory security impression marks. This concentration can be raised to about 20% or 30%, depending on the degree of solubility of the chemical in a particular solvent, and the viscosity of the resulting liquid composition, which may affect handling, as previously discussed. In general, concentrations substantially below 5% will not lead to the good results obtained with higher concentrations. It has been found that a large variety of these ultraviolet absorbent organic chemicals may be used to make the security impressions, so long as the chemical is compatible with the paper for the intended purpose, that is, it dries to an invisible or virtually invisible mark and does not discolor or provide any substantial telltale signs in the dry state. Likewise, the chemical must be compatible in the sense that it is ink-receptive and preferably useful over extended periods of time so that it can be subjected to repeated steps of exposure upon wetting, disappearance upon drying, and re-exposure upon re-wetting.

A large variety of organic solvents can be used to prepare the liquid composition with the ultraviolet ab-

sorbing chemical. They may include the various glycol ethers, such as ethylene glycol monomethyl ethers and the corresponding dimethyl ethers, monoethyl ethers, diethyl ethers, monobutyl ethers, monohexyl ethers, and the like.

The diethylene glycols are also useful, such as diethylene glycol monomethyl ether, and the corresponding monoethyl ethers, monobutyl ethers and diethyl ethers. Other solvents which are useful are dimethyl formamide, triacetin, N-butyl acetate, monoethyl ether acetate, cyclohexanone and the like. The solvent selected has only a few requirements to meet operability, namely, its ability to dissolve the ultraviolet absorbing organic chemical, its volatility so as to allow convenient removal after application by evaporation, heat, passage of warm air or the like, and its compatibility with the paper. By "compatibility" is meant that the organic solvent does not adversely affect the paper by discoloring it or leaving other telltale signs after removal following application. Likewise, the organic solvent should not damage the paper by any substantial weakening of the fibers, caustic action or the like.

In the following table, a representative number of examples are summarized wherein various ultraviolet absorbing chemicals in a liquid composition are applied to the surfaces of finished papers. The organic solvent liquid composition is methyl "Carbitol" (diethyleneglycol methyl ether) and the ultraviolet absorbing organic chemicals are present therein, in a concentration of about 10% by weight. Such a liquid composition is contacted with an elastomeric hand stamp, and the wetted hand stamp is then contacted with a portion of the surface of the finished paper. The security impression is allowed to dry by evaporation of the organic solvent. All of the security impressions in the dry state were invisible, or virtually invisible, and were distinctly visible after wetting the paper with water. The results of artificially aging the papers with the security impression marks are summarized.

TABLE I

Material tested	Security mark's visibility		Ink feathering
	Fadeometer	Oven age	
Eastman Inhibitor HPT	Visible	Visible	None.
Eastman Inhibitor DHPB	do.	do.	Do.
Eastman Inhibitor OPS	Slightly visible	Slightly visible	Do.
Eastman Inhibitor RMB	Visible	Visible	Do.
Univul M-40	Slightly visible	Slightly visible	Do.
Univul N-35	do.	Very slightly visible	Do.
Univul MS-40	do.	Slightly visible	Do.
Univul 400	Visible	Visible	Do.
Agent AT-539	Slightly visible	do.	Do.
CYASORB UV-9	do.	do.	Do.

The indications under the "Fadeometer" heading report the appearance of the re-wetted mark after six hours in the Fadeometer. The Fadeometer is a well-known instrument for comparing the fading properties of different materials, which are exposed under standard conditions of humidity and the like to a carbon arc which operates as artificial sunlight. The designations under the column entitled "Oven Age" report the appearance of the mark after the paper has been re-wetted following 72 hours in an oven at 105° C. The ink feathering column indicates that the mark has excellent ink receptivity in that none of the ink feathers or blurs on the portion of the paper where the security impression has been applied.

The following Table II indicates various concentrations of the ultraviolet absorbing chemicals which were used to make security impressions by applying a liquid composition containing the material in the stated amount dissolved in methyl "Carbitol" solvent. The security impression mark formed was satisfactory in that it was invisible or virtually invisible to the casual observer in the dry state, and was visually detectable after wetting the paper with water.

TABLE II

	Ultraviolet material	Percent by weight of material in methyl Carbitol solvent
Eastman Inhibitor.....	DHBP	6
Do.....	OPS	22
Do.....	RMB	6
Uvinul.....	M-40	22
Do.....	N-35	22
Do.....	MS-40	22
Do.....	400	6
Cyasorb.....	UV-9	22

In the practice of this invention, the security impression mark can be applied to the surface of the finished paper product or sheet before the conventional visual impressions are applied, or after such conventional visual impressions are applied. The conventional visual impressions referred to include handwriting by pencil, ink or the like; and printing with various printing inks known in the art. This security impression mark can be applied to a portion of the paper surface spaced away from the conventional impression marks, or can be applied to an area of the paper where the conventional impressions have been or will be applied.

If the conventional impressions are of the permanent type then, of course, the paper can be repeatedly wetted and dried to check the paper for reappearance of the security mark. This will check its authenticity, its source, or whatever information the appearance of the security impression or mark will convey to the user. If the conventional visual impressions are smeared, blurred or otherwise defaced by water, it will clearly not ordinarily be reusable, but the reappearance of the security pressure mark in a wetted state will still have served a useful purpose.

The security impression mark can be applied in any one of many selected designs or configurations. Such will be meaningful in the sense that they will authenticate or check out the paper product. It will be appreciated that particularly fanciful or distinctive security impressions may be preferred to customize certain papers, or to code them, or to enumerate them in a series or program. All such advantages may be realized in the practice of the present invention.

I claim:

1. A method for preparing a security paper product with security impressions which includes the steps of: applying to the surface of a finished sheet of paper a liquid security composition to form a non-continuous impregnation of the sheet, said composition including an ultraviolet inhibitor comprising an ultraviolet absorbing organic chemical selected from the group consisting of 2 - hydroxy - 4 - methoxybenzophenone; ethyl - 2 - cyano - 3, 2 diphenyl acrylate; 2 - hydroxy - 4 - methoxybenzophenone-5-sulfonic acid; 2,4 - dihydroxybenzophenone; 2 - ethyl hexyl - 2 - cyano - 3, 3 diphenyl acrylate; hexamethylphosphoric trianide; resorcinol monobenzoate; 4-dodecyl-oxy - 2 - hydroxybenzophenone; and p - octylphenyl salicylate and an organic chemical solvent, said ultraviolet absorbing organic chemical applied in an amount to be invisible upon subsequent removal of the solvent and visually detectable upon wetting the paper with water, and removing the organic solvent to obtain a dry security impression.
2. A method as in claim 1 further characterized by and including the step of initially applying normally visible impressions to the surface of the paper which serve a desirable meaningful purpose, and then applying the security composition to a selected portion of the paper.

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S. LEON BASHORE, Primary Examiner

T. G. FERRIS, Assistant Examiner

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162—140, 158