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㉙ Security paper containing vesiculated beads.

㉚ Security paper contains polymeric vesiculated beads having a volume average particle size of at least about 10 microns up to about 35 microns, these beads containing dye or pigment which glows when irradiated with nonvisible radiation, and being hard to see when the paper is viewed with the naked eye under normal visible light.

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SECURITY PAPER CONTAINING
VESICULATED BEADS
DESCRIPTION

Technical Field

5 This invention relates to security paper containing vesiculated beads which are not visible when viewed by visible light, but which are easily seen when exposed to nonvisible radiation.

Background Art

10 Special papers have been developed for security purposes to help insure that the document is genuine. These papers are illustrated by the use of colored fibers, planchettes, water marks or special dyes. It is desired to provide papers which will be
15 more difficult for the counterfeiter to duplicate. The special character of some of these papers is easily seen by close inspection under ordinary light, so anyone viewing the paper is alerted to the need for using a paper having a special appearance, and it
20 is not too difficult to provide a duplicate paper. In some instances a special light is needed to see a dye in the paper, but it is still not too difficult to provide a paper containing a comparable concentration of the same dye. It is desired to
25 provide security paper which contains very easily visible identification when viewed by nonvisible light, whereas this identification is not visible when the paper is viewed under normal lighting. In this way, one attempting to mimic the document may
30 not be alert to the fact that ordinary paper cannot be used. Moreover, it is desired to provide paper which is not easily duplicated even when the party attempting to mimic the document is alert to the fact that the paper has a peculiar appearance under
35 nonvisible light.

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It is also important to provide a paper which is economically producible, which is printable, as by engraving processes, without damage, and which can be viewed to insure its genuine nature from either side of the paper.

Disclosure of Invention

In accordance with this invention, there is incorporated into the paper furnish, cross-linked, polymeric vesiculated beads having a volume average particle size of at least about 10 microns, preferably at least 20 microns, up to about 35 microns, and which include pigment or dye which responds to nonvisible radiation, especially to ultraviolet light. These polymeric vesiculated beads are small enough so that they are not visible to the unaided eye, even when these beads are colored when so viewed and incorporated into white paper. However, under nonvisible light, these beads glow and provided bright spots (which may have a distinctive coloration or combination of colorations) to identify the paper and distinguish it from ordinary paper as well as other special papers having a different density of bright spots and/or spots of different coloration.

In preferred practice, the security paper will contain from 0.1 to 15 weight percent of such beads, preferably from 0.5 to 5% thereof, based on the total weight of the paper. This paper may be calendered or uncalendered.

It is desired to point out that prior security papers are frequently single sided in that the fibers or other identifying devices concentrate at the wire side of the paper. In this invention, the beads which are incorporated in the paper become visible under nonvisible light at both sides of the

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paper, and this eases the burden of examination.

It is stressed that the vesiculated beads under consideration contain many cells and are quite different from ordinary hollow polymer beads in being
5 load bearing. As a result, these beads can be present in paper which sustains the pressure of the calendering and engraving processes which are involved in the production of security papers.

The beads under consideration normally
10 contain an average of at least about 5 cells per bead, preferably at least about 10 cells per bead. It appears that the presence of a large number of cells in each bead is what allows the bead to avoid collapse when paper containing the same is compressed
15 under the considerable force imposed in the calendering operation.

It is stressed that the beads in this invention have transparent walls, and the multiplicity of cells retroreflects the incident
20 light to produce a very bright spot of emitted light when the paper is appropriately irradiated. It is very difficult to duplicate the brightness of the vesiculated beads using plastic beads of different character. Moreover, the most effective way to
25 provide the beads which are used herein is to incorporate the pigment or dye into the cell walls at the time of their production, and it would be very difficult to add a corresponding coloration after the beads have been formed. It is unlikely that one
30 attempting to duplicate a security paper would be able to mimic the beads which are used herein.

It is also stressed that the appearance of invisibility in ordinary light and easy visibility in nonvisible light is an aspect of the fact that the
35 beads are uniformly distributed throughout the body

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of the paper. This uniform distribution of the beads throughout the body of the paper requires that the vesiculated beads be added to the paper furnish. It is found that when the beads are so added, they are
5 effectively retained in the paper as the water and some of the fines and mineral filler used in papermaking pass through the Fourdrinier wire in conventional papermaking.

Bead retention can be enhanced when
10 conventional retention aids are employed, though this is not essential. Both anionic and cationic retention aids are useful, but anionic retention aids are more efficient. The vesiculated beads are distributed quite uniformly throughout the paper and,
15 while many of them are buried within the paper so as to be invisible on casual inspection, they will nonetheless pick up nonvisible light and glow in the visible range to provide a bright spot which is easily seen.

20 The retention aids which have been found to be useful herein are themselves well known, and many are available in commerce. Acrylamide and methacrylamide copolymers with monoethylenic acids or monoethylenic amines are preferred, these generally
25 containing from 5% to 50% of the acid or amine monomer, balance the amide monomer. The anionic copolymers which are preferred will usually contain acrylic or methacrylic acid as the acid component, and these are rendered anionic with the aid of an
30 amine, which is preferably ammonia. Thus, a copolymer of 20% methacrylic acid with 80% acrylamide is illustrative of a preferred anionic retention aid.

The cationic amide copolymers are illustrated by copolymers of acrylamide with diethyl
35 aminoethyl methacrylamide.

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Various other anionic and cationic resins which may be used as the retention aid are discussed in the Kirk Othmer "Encyclopedia of Chemical Technology, third edition" Volume 16, at page 804
5 which points out that the usual fillers having a size up to 5 microns are not effectively retained because they are so small, thus provoking the use of retention aids in the paper furnish. The beads used herein are generally much larger, but their retention
10 on the Fourdrinier wire is enhanced by the conventional retention agents nonetheless.

The preferred vesiculated beads are styrene-cross-linked unsaturated polyester resins. These are made into a vesiculated bead in
15 conventional fashion, as illustrated by U.S. Pat. No. 3,879,314. The size of the vesiculated beads under consideration may vary considerably, but is generally larger than a volume average of about 10 microns in diameter. For example, beads having a volume average
20 diameter of from about 10 to about 35 microns are conveniently prepared and fully useful in this invention. As the bead size increases above about 20 microns, they become particularly easy to see when properly exposed, and are thus preferred for use
25 herein.

Various other patents are of interest to the formation of vesiculated beads useful in this invention, particular attention being directed to U.S. patents Nos. 3,822,224, 3,923,704 and
30 3,933,579. This last-named patent describes the vesiculated beads which are preferred herein, namely, those having a ratio of granular diameter to mean vesicle diameter of at least 5:1, a vesicle volume of from 5% to 95% of the volume of the granule, and not
35 more than about 60% pigment, by volume.

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The vesiculated beads used herein have a highly cross-linked polymeric body which is preferably constituted by a carboxyl-functional unsaturated polyester resin cross-linked with an ethylenically unsaturated monomer copolymerizable therewith. The unsaturation in the polyester is preferably maleate unsaturation, these polyesters being themselves well known and illustrated hereinafter. It is preferred that the polyester have an acid value of 10 to 45 mgm KOH per gm.

The unsaturated monomers used for cross-linking are also well known and are water insoluble monomers typically illustrated by styrene or vinyl toluene. The polyesters and monomers are more fully discussed in U.S. Pat. No. 3,879,314 which shows the production of vesiculated beads using a water-soluble polyamine containing at least three amine groups per molecule and having a dissociation constant in water (pKa value) of 8.5-10.5, typically illustrated by diethylene triamine. The polyamine is used in a concentration providing at least 0.3 amine groups per polyester carboxyl group, usually from 0.5 to 1.4 amine groups per polyester carboxyl group. It is preferred to have from 35% to 45% of the unsaturated polyester cross-linked with from 55% to 65% of styrene.

The invention is illustrated as follows, it being understood that all parts and proportions are by weight, unless otherwise specified.

30 Example

Suitable pigmented vesiculated beads in accordance with this invention are illustrated in U.S. Patent No. 3,879,314 issued April 22, 1975, see particularly Example II. By proceeding in accordance with said Example II and using a polyester of 18%

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phthalic anhydride, 37% maleic anhydride and 45% propylene glycol dissolved in styrene to form a solution containing 41.8% of the polyester, vesiculated beads pigmented with a pigment which glows when irradiated with ultraviolet light, to contain about 19.0% pigment, by volume, are provided. These beads have an average size of about 25 microns and contain an average of more than 10 cells per bead.

These beads are typically incorporated into a paper furnish in which 800 pounds per ton of softwood kraft, 1200 pounds per ton of hardwood kraft, 300 pounds per ton of clay, 20 pounds per ton of rosin size, and 30 pounds per ton of alum are mixed into water to a consistency of about 3%. The pH is adjusted to a pH in the range of 4.5 to 6.5 by the addition of concentrated sulfuric, and this provides the furnish which is modified by the addition of beads in this invention. The above proportions are in pounds per ton of finished paper basis. This furnish is modified to include 4% or 6% of the vesiculated beads and 1.5% of titanium dioxide, anatase, based on solids content and is supplied to the head box by passing the mixture through a valve in which the solids concentration is reduced to 1.5%.

The paper made from this bead-containing furnish had a basis weight in the range of 37 to 40 pounds per ream, and it was passed through a size press in conventional fashion and then calendered at either 150 or 900 pounds per linear inch at a temperature of about 150°F. to provide a printable paper. This paper, when viewed with ordinary light, appeared to be an ordinary paper, but when viewed with ultraviolet light was seen to have glowing spots all over it, like salt scattered on black paper.

1. A security paper containing polymeric vesiculated beads having transparent walls and a volume average particle size of at least about 10
5 microns up to about 35 microns, said vesiculated beads containing dye or pigment which glows when irradiated with nonvisible radiation, and said vesiculated beads being hard to see when the paper is viewed with the naked eye under normal visible light.

10 2. A security paper as recited in claim 1 in which said vesiculated beads have a volume average particle size of at least about 20 microns.

3. A security paper as recited in claim 1 in which said vesiculated beads are present in an
15 amount of from 0.1% to 15% and contain an average of at least 5 cells per bead.

4. A security paper as recited in claim 3 in which said vesiculated beads have a ratio of granular diameter to mean vesicle diameter of at
20 least 5:1, a vesicle volume of from 5% to 95% of the volume of the granule, and not more than about 60% pigment, by volume.

5. A security paper as recited in claim 1 in which said vesiculated beads are incorporated in
25 the furnish to be relatively uniformly distributed throughout the body of the paper.

6. A security paper as recited in claim 5 in which said paper is calendered.

7. A security paper as recited in claim 5
30 in which the polymeric body of said beads is constituted by a carboxyl-functional unsaturated polyester resin cross-linked by an ethylenically unsaturated monomer copolymerizable therewith.

8. A security paper as recited in claim 7
35 in which from 35% to 45% of unsaturated polyester

containing maleate unsaturation is cross-linked with
from 55% to 65% of styrene.

9. A security paper as recited in claim 1
in which said pigment or dye is associated with the
5 walls of said cells.

10. A security paper as recited in claim 1
in which said vesiculated beads are present in an
amount of from 0.5% to 5%.

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European Patent
Office

EUROPEAN SEARCH REPORT

0219743
Application number

EP 86 11 3634

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
Y	FR-A-2 478 695 (AUSSEDAT REY) * Claims 1-5,8 *	1,3,5,9	D 21 H 5/10
Y	--- GB-A-1 528 193 (HOECHST) * Whole document *	1-3,10	
D,Y	--- US-A-3 933 579 (R.W. KERSHAW et al.) * Examples 7,29; column 3, lines 26-52 *	1-3,5,9,10	
A	-----	4,7,8	
			TECHNICAL FIELDS SEARCHED (Int Cl 4)
			B 44 F D 21 H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-01-1987	Examiner NESTBY K.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	