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(54) Printing process using acetylenic compositions.

(57) Acetylenic compound having at least two conjugated triple bonds in the molecule and polymerizable in the cyrstalline solid state to produce coloration, but relatively stable in liquid form, and having substituents of the group consisting of urethane, hydroxy, carboxy, carboxylic acid, carboxylic ester, carbazolyl and sulfonate, are used as printing ink. Preferred compounds are diynes, especially urethanes, diols and arylsulfonates melting in the range 40-150°C. They are employed as a melt at 40°-200°C adhering to the printing surface, whence they are transferred by contact to a substrate; and developed by cooling and exposure to a source of thermal or radiation energy.

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DESCRIPTION

PRINTING PROCESS USING ACETYLENIC COMPOSITIONS

BACKGROUND

A number of printing process are known wherein a liquid serving as an ink is transferred to a substrate such as paper or plastic upon which the printed matter is to appear, by use of a printing form with raised surfaces (letterpress) or with grooved surfaces (gravure) or with oleophilic and oleophobic surfaces obtained by photo action (planographic or offset) or with a stencil formed by a screen (screen printing). The conventional inks used in such processes in general are composed of a resinous binder, a pigment, a solvent, and various additives. More recently, inks have been produced which are in the form of organic polymers having the desired viscosity and curable by ultraviolet radiation. These inks are based, for example, upon acrylic esters.

Certain acetylenic compounds are known, polymerizable in the solid state as such and/or in admixture by heat and/or by ultraviolet radiation or other high energy radiation, which compounds become colored upon solid state polymerization.

These acetylenic compounds have at least two conjugated triple bonds in the molecule. Characteristically, they are stable against polymerization when in liquid forms, dissolved or fused. Such compounds are disclosed for example in USP 3,999,946 of December 28,

1976 to Patel et al. In particular, that patent discloses at column 7, line 39 to column 8, line 5 that the acetylenic compounds of that invention are substantially inactive in solution and in molten state; and that deposition as a solid on a substrate from solution or melt phase results in an active phase that changes color in response to time/ temperature exposures and in some cases also to exposure to short wave length UV or UV-visible radiation.

USP 3,501,302 of March 17, 1970 to Foltz discloses forming images by exposure to radiant energy of a carrier means having thereon a coating containing radiant energy sensitive solid crystalline acetylene composition of matter wherein the acetylene compound contains at least two conjugated triple bonds, and the print out image is of a color distinctly different from that of unexposed portions of the coated carrier.

None of the above art teaches a process whereby an acetylenic composition can be employed for printing in the manner of an ink.

SUMMARY OF THE INVENTION

The present invention provides a printing process using fusible acetylenic compound having triple bonds in the molecule, at least two of which bonds are conjugated; said compound being polymerizable in the solid state but stable against polymerization when in liquid form; which process consists essentially of the steps:

(a) applying to a heated printing head, to thereby form a liquid carried thereon, an acetylenic composition consisting essentially of at least one substituted acetylenic compound containing at least two conjugated triple bonds and having at least one substituent wherein at least one methylene radical links a carbon atom, having such conjugated triple bond, to a radical selected from the group consisting of urethane, hydroxy, carboxy, carboxylic acid, carboxylic ester, carbazolyl, and sulfonate; said printing head having

areas thereof designed and adapted for release of liquid, carried by said head, upon contact with a sub-substrate;

(b) by contact between said printing head and a substrate, transferring liquid from said areas of said head carrying liquid, to said substrate;

(c) causing said liquid to cool whereby to deposit said acetylenic composition in a solid form active for solid state polymerization by thermal energy or by radiation energy;

(d) exposing said active solid acetylenic composition to at least one source of thermal energy or radiation energy, of intensity and duration at least sufficient to effect partial polymerization and accompanying coloration of said active acetylenic composition.

Particular advantages of the present process include the fact that because no volatile solvent is needed, serious problems of the printing art, namely atmospheric pollution and need to recover a solvent, are avoided in this process.

It will be appreciated that the choice of possible acetylenic compounds is wide but must be confined to such compounds as are stable in the liquid form and, when cooled, deposit the acetylenic composition as a solid which is polymerizable by heat or by radiation in a reasonably short time to produce an adherent deposit on the substrate, occupying the exact area corresponding to the printing area of the printing head. For this purpose, the acetylenic compound should have substituents above specified, we have found, and the substrate should have an affinity for the liquid acetylenic compounds. If the substrate is naturally repellent toward the liquid, it can be treated in known manner to improve the affinity, e.g. as is done with polyethylene to make it printable to conventional inks.

DETAILED DESCRIPTION

Preferred substituents in our acetylenic compounds for use as printing inks are urethane, hydroxy or arylsulfonate, and preferably the composition consists essentially of one or more symmetrical diynes having melting point of 40-150°C and is employed as a melt at temperature in the range between 40 and 200°C.

Representative acetylenic compounds which can be used in our compositions are the urethanes given in Table 1.

TABLE I

1. Monomers

(A) $RNHOCO-(CH_2)_n-C\equiv C-C\equiv C-(CH_2)_n-OCONHR'$

n	R=R'	Melting Point (°C) (By DEC Method)
4	ethoxycarbonylmethylene	82.5-83
"	n-butoxycarbonylmethylene	74
"	m-tolyl	110
"	p-tolyl	163
"	o-chlorophenyl	102
"	2-chloroethyl	106
"	p-bromophenyl	158
3	ethoxycarbonylmethylene	83
"	n-butoxycarbonylmethylene	67
"	m-tolyl	93
"	m-chlorophenyl	95
"	p-chlorophenyl	150
"	hydroxy	45
2	m-tolyl	136
"	m-methoxyphenyl	141
"	p-methoxyphenyl	206
1	ethyl	95
"	n-butyl	78

When "radiation energy" is referred to herein, it is to be understood that this term embraces actinic radiation and infrared radiation and also electron beams such as developed by cathode ray guns; gamma rays; X-rays; beta rays; corona discharge; and the like.

Preferred acetylenic compounds and preferred temperature ranges for their use as melts have been cited above. The optimum choice of compound or mixtures of compounds and temperature of heating the same will obviously vary with the specific type and construction material of the printing head and material of the substrate. The characteristics of compositions of this invention can be varied accordingly, with respect to such factors as viscosity, adherence to the printing head and to the substrate, and coherence of the liquid by varying the choice of acetylenic compound and/or the temperature of use; by including in varying proportions a second acetylenic compound in the composition; and/or by use of additives such as a binder, a plasticizer, a UV stabilizer or a solvent. The use of such additives, however, is preferably avoided in order to simplify the procedure.

Particularly preferred compounds are illustrated by the following Examples.

PROCEDURE

In the Examples, a monomeric diacetylene powder was thinly coated on a piece of filter paper. The monomer was melted by heating the paper from the bottom to provide an ink pad for purposes of testing operativness of several representative compounds as shown in the Examples. A rubber stamp was contacted with the molten diacetylene on the filter paper thereby applying a thin coating of melt to the stamp. The melt was then transferred from the printing areas of the stamp to a piece of filter paper by pressing the stamp against the paper.

As the melt cooled upon the paper it crystallized to solid monomer, leaving a colorless or slightly colored impression of the stamp on the paper. The paper was then exposed to heat or to UV (ultraviolet) light (as indicated in the Examples) whereby the impression of the stamp appeared in readily legible letters upon the paper.

If necessary, the rubber stamp was heated or reheated with a hot air gun to prevent premature crystallization of the diacetylene monomer on this stamp.

EXAMPLE 1

The diacetylene, 5, 7-dodecadiyn-1,12-bis (n-butoxycarbonylmethylene urethane) wherein R,R'= $-(CH_2)_4OCONHCH_2COO(CH_2)_3CH_3$ was used as ink. The monomer was melted on a piece of filter paper by heating at 80°C. Using the procedure described above an invisible impression of the rubber stamp was obtained on paper. Upon a brief exposure to UV light, the visible impression of the stamp was obtained in blue color. Upon exposure (ten seconds) the monomer polymerized further and a metallic (copper colored) impression of the stamp was obtained. The diacetylene has reasonable adhesion with the paper. On rubbing with the hand no smearing was noted.

EXAMPLES 2-6

Several other diacetylenes were tested on the ink formulations using the procedure described above. The diacetylenes, methods of polymerization and colors upon polymerization are indicated below.

"A"

Ex.	Diacetylene R-C=C-C=C-R	R	M.P. (°C)
2	diol	$-(CH_2)_3OH$	45
3	bis(n-butyl urethane)	$-CH_2OCONHC_4H_9$	78
4	bis(p-toluene sulfonate)	$-CH_2O(SO_2)C_6H_4CH_3$	98
5	bis(ethyl urethane)	$-CH_2OCONHC_2H_5$	95
6	mixture of 3 and 5 above, cocrystallized	80:20 by wgt.	-

"B"

Ex.	Means of Polymerization	Initial Color	Final Color
2	UV	Blue	metallic
3	UV	Red	copper metallic
4	Thermal	Red	green gold
5	UV	Red	dark red
6	UV	Purple	green gold

EXAMPLE 7

1. Synthesis of 9-(N-carbazolyl)-5,7-nonadiyn-1-ol

To a 100 ml, 3 necked flask, fitted with mechanical stirrer, addition funnel, thermometer and reflux condenser, was charged at room temperature, 3.6 grams (0.012 mol) 9-(N-carbazolyl)-5,7-nonadiyn-1-ol (synthesis of this compound has been described in U.S.P. 4,125,534), 10 ml 1,2-dimethoxyethane (glyme) 0.1 gram dibutyltin-di-(2-ethyl) hexanoate, and 1 ml triethylamine, under a nitrogen atmosphere. To the stirred mixture, was added a solution of 2.2 grams (0.018 mol) phenylisocyanate and 10 ml glyme in one portion. The reaction temperature rose to 35°C in about 5 minutes and then subsided to 25°C. The reaction mixture was stirred at 45°C for an additional 3 hours and then cooled to room temperature. Heptane, 80 ml, was added in one portion, resulting in a white precipitate. The precipitate was collected by filtration and washed with heptane and petroleum ether. Obtained was 4.1 grams of a white solid, representing an 82% yield of theory of the desired compound possessing a melting point of 123.5° to 124.5°C.

2. Active and Inactive Forms

Recrystallization of the above obtained solid from acetone yielded two crystal forms: "A", white platelets, having a melting point of 124.5° to 125°C., which were inactive towards 1,4-addition polymerization upon exposure to a total of 50 Mrads of gamma radiation; and "B", red needles, having a melting point of about 145°C, which evidenced a color change to metallic green-

gold upon exposure to a total of 50 Mrads of gamma radiation. "A" is an inactive form and "B" is an active form.

Elemental analysis of both compounds showed that they both were of the same empirical formula, calculated for the formula $C_{28}H_{24}N_2O_2$; %C (calculated) 79.98; % H 5.75 (calculated); for "A", % C (found) 79.93, % H (found) 5.81; for "B", % C (found) 79.96, % H (found) 5.59.

The X-ray powder diffraction patterns for the inactive form "A" and the active form "B", respectively, show that they exist in separate and distinct crystalline forms.

3. Conversion

It was found that by heating the inactive white platelets at a temperature of about 127°C a melt was formed, which when slowly cooled by allowing to stand at room temperature, resulted in the active form "B". Such melt can be formed as a coating on a piece of filter paper, as in Example 1, and transferred to a printing head and to paper and exposed to radiation to form a printout as in Example 1.

EXAMPLE 8

The monomethyl ester of 10,12-docosadiyndioic acid is prepared as described in Example N at col. 15-16 of U.S.P. 3,501,302 of Mar. 17, 1970, having melting point of about 60-62°C. As disclosed in Example 12 of that patent (Col. 24) this acetylenic compound, when exposed in crystalline form to ultraviolet radiation, changes to a blue color; whence it follows this compound can be employed in melt form as an ink by the general procedure of Example 1 above.

EXAMPLE 9

11,13-Tetracosadiyndioic acid product of Example 1 at col. 21 of U.S.P. 3,501,302 of M.P. 118°C is applicable in the present invention similarly to the monoester of Example 8.

It will be appreciated that the above examples

represent just a few of the many diacetylene compositions, and compositions containing additional conjugated or non-conjugated triple bonds, which are operative in the process of this invention and which melt within a convenient range and solidify on cooling in place or by forced cooling to deposit an active solid acetylenic composition in areas of the substrate which correspond accurately to the printing areas of the printing head employed.

It will be appreciated also that the acetylenic compounds or compositions used as inks in the process of this invention can be used to print one part of a label, to serve, say, as an indicator; and another part can be printed using a conventional ink. For example a message such as "STALE-DISCARD" can be applied to a label, using an acetylenic ink such as that of Example 4 hereof in colorless form, and will become visible in say red after sufficient exposure to the combined effects of temperature and time, or to the effects of radiation. If desired, the customary labeling information can be printed on the same label using a conventional ink.

Claims:

1. A printing process using a fusible acetylenic compounds having triple bonds in the molecule, at least two of which bonds are conjugated; said compound being polymerizable in solid state but stable against polymerization when in liquid form; consisting essentially of the steps

(a) applying to a heated printing head to thereby form a liquid carried thereon, an acetylenic composition consisting essentially of at least one substituted acetylenic compound containing at least two conjugated triple bonds and having at least one substituent wherein at least one methylene radical links a carbon atom, having such conjugated triple bond, to a radical selected from the group consisting of urethane, hydroxy, carboxy, carboxylic acid, carboxylic ester, carbazolyl, and sulfonate; said printing head having areas thereof designed and adapted for release of liquid, carried by said head, upon contact with a substrate;

(b) by contact between said printing head and a substrate, transferring liquid from said areas of said head, carrying liquid, to said substrate;

(c) causing said liquid to cool whereby to deposit said acetylenic composition in a solid form active for solid state polymerization by thermal energy or by radiation energy;

(d) exposing said active solid acetylenic composition to at least one source of thermal energy or radiation energy, of intensity and duration at least sufficient to effect partial polymerization and accompanying coloration of said active acetylenic composition.

2. Process in accordance with claim 1 wherein such substituent of such substituted acetylenic compound is urethane, hydroxy or arylsulfonate.

3. Process in accordance with claim 2 wherein such substituted acetylenic compound is a symmetrical diyne and is employed as a melt at temperature in the

range between 40 and 200°C.

4. Process of claim 1 wherein the acetylenic composition consists essentially of 5,7-dodecadiyn-1,12-bis(n-butoxycarbonylmethylene urethane).

5. Process of claim 1 wherein the acetylenic composition consists essentially of 4,6-decadiyn-1,10-diol.

6. Process of claim 1 wherein the acetylenic composition consists essentially of 2,4-hexadiyn-1,6-bis(n-butyl urethane).

7. Process of claim 1 wherein the acetylenic composition consists essentially of 2,4-hexadiyn-1,6-bis(ethylurethane).

8. Process of claim 1 wherein the acetylenic composition consists essentially of 2,4-hexadiyn-1,6-bis(p-toluene sulfonate).

9. Process of claim 1 wherein the acetylenic composition consists essentially of 80 parts by weight of 2,4-hexadiyn-1,6-bis(n-butyl urethane) cocrystallized with 20 parts of 2,4-hexadiyn-1,6-bis(ethyl urethane).