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3,823,034

ELECTRO-SENSITIVE RECORDING BLANK

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46/77,326

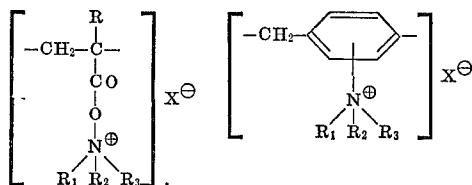
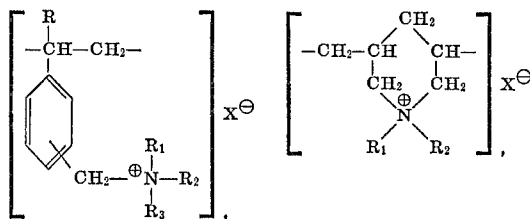
Int. Cl. B41c 3/08; B44d 1/18

U.S. Cl. 117-218

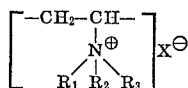
7 Claims

ABSTRACT OF THE DISCLOSURE

The electro-sensitive recording blank comprises a backing layer of paper, an electro-conductive dark-colored coating on said backing layer and a white surface coating on said dark-colored coating, said white surface coating including a white pigment, a binder and at least one polymer, said polymer comprising at least one kind of monomer unit which is selected from the group consisting of monomers represented by the following formulas:



and



wherein R is hydrogen or alkyl having 1-4 carbon atoms, each of R₁, R₂ and R₃ is alkyl, at least one of R₁, R₂ and R₃ is alkyl having at least 10 carbon atoms, and X[⊖] is anionic radical.

BACKGROUND OF THE INVENTION

This invention relates to an electrosensitive recording blanks for recording characters, graphic patterns or the like in a visible form through electric signal.

Generally, electrosensitive recording blanks comprise a base sheet of paper, plastic film or the like, a colored electroconductive layer coated on a surface of said base sheet and a white marking layer of low electrical resistance covered on said colored electro-conductive layer. The colored electro-conductive layer is formed by coating on the base sheet with a coating composition consisting of a mixture of deep colored electro-conductive carbon black with a binder and in some cases further depositing vaporized metal on the thus formed coating layer in order to obtain a good contrast of the recorded image and to get a sufficient electroconductivity as a return path for electric charge. The white marking layer of low electrical resistance is formed of a coating composition comprising burnt or annealed fine particles of zinc oxide, titanium dioxide and etc. and a binder. These recording sheets make a permanent visible image on their surface upon receipt of electric signals through a recording stylus which is contact with the white marking layer, with said

white marking layer being partially broken to expose the inner dark or black conductive coating layer. These recording sheets find their particular usefulness in facsimile recording system science; the developing and fixing processes are omitted and the entire equipment system is simpler. However, these recording sheets have a number of disadvantages of accompanying with odors or dusts upon the recording, of giving lower contrast of recording images, of narrower allowance of the recording conditions, and of higher material cost. The function of electrosensitive recording is to break the white marking layer under high electric field of signal potentials for exposing the visible image. It evolves to subsequently break the conductive colored layer. The threshold voltage becomes higher as the difference of electric resistance between conductive colored layer and white marking layer becomes greater. And the more the power consumption is, the more odor and dust accompany the process. For this reason annealed titanium dioxide, zinc oxide, zinc sulfide and cadmium sulfide powder had so far been used to reduce the electric resistance of the marking layer. But, it was very difficult to obtain the marking layer having a reduced resistance as desired even with use of such annealed zinc oxide and other inorganic powder materials. It was also difficult to obtain a good black-and-white contrast of images since those powders are generally colored by burning. The allowance of recording conditions becomes narrower when threshold voltage is high, while the practical allowance would be able to considerably expand if the recording sheet is highly sensitive and of low power consumption.

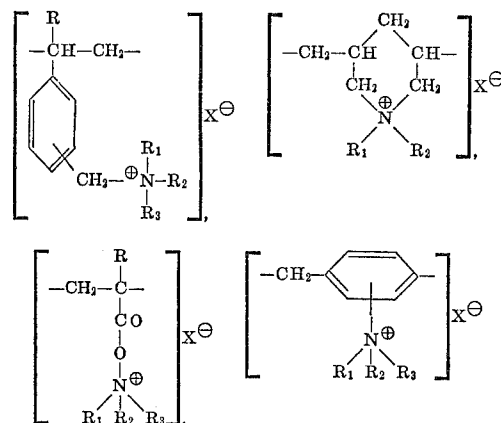
The principal object of the invention is to provide an improved recording blank capable of recording at a low voltage, in which the outer white has a reduced electrical resistance so that the difference in the electro-conductivity between the under layer and the white marking layer may be reduced.

Another object is to provide a recording blank which scarcely involves production of odors and dusts during recording operation.

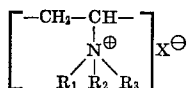
A further object is to provide a recording blank capable of obtaining high-contrast, sharp images.

SUMMARY OF THE INVENTION

The electro-sensitive recording blank according to the invention comprises a backing layer of paper, a dark-colored coating on said backing layer and a white surface coating on said dark-colored coating, said white surface coating including a white pigment, a binder and at least one polymer, said polymer comprising at least one kind of monomer unit which is selected from the group consisting of monomers represented by the following formulas:



and



wherein R is hydrogen or alkyl having 1-4 carbon atoms, each of R₁, R₂ and R₃ is alkyl, at least one of R₁, R₂ and R₃ is alkyl having at least 10 carbon atoms and X[⊖] is anionic radical. All of R₁, R₂ and R₃ may be alkyl having at least 10 carbon atoms, but the remaining one or two of R₁, R₂ and R₃ may be lower alkyl. Among alkyl groups with more than 10 carbon atoms (preferably C₁₂-C₂₂), there may be included lauryl, myristyl, palmityl and stearyl and among lower alkyl, groups there may be included methyl, ethyl and n-propyl. For X[⊖] a quaternary ammonium salt, any of halogen ions (Cl⁻, Br⁻, and I⁻) and alkyl sulfate anion (CH₃SO₄⁻) may be used. The polymers used in this invention may be copolymers of the above-mentioned monomers with the other monomers such as aromatic vinyls, vinyl esters and vinyl ethers.

Since at least one of R₁, R₂ and R₃ is long-chained alkyl having more than 10 carbon atoms, the white marking layer is hardly accompanied by odor development during the process of decomposing at a recording stage. By selecting an optimum number of carbon atoms at from 10 to 22, these polymers can be solubilized in organic solvents such as alcohol and ketones. Since the polymers utilized in this invention are of low electrical resistance, the resultant product requires a reduced power consumption and is active at a reduced threshold voltage.

The above-mentioned polymers can be handled in the condition of aqueous base or solvent base. A coating color composition containing any of these polymers, a white pigment such conventional zinc oxide and titanium dioxide and a natural or synthetic binder can be applied to a base sheet having a colored conductive layer to form white marking layer by means of conventional coater.

The content ratio of polymers in the coating color composition is not specifically limited but is preferably within the range of 1 to 30 weight percent of the total weight of the white pigment and the binder resin when desired decrease of electrical resistivity and opacity of white marking layer are taken into consideration.

The degree of molecular weight of the polymers is not specifically restricted so long as it has a viscosity which enables practical handling, but it may preferably be within the range of about 1,000 to 100,000. The base sheet may be selected from cellulose matrix sheet, plastic film sheet or synthetic paper, and colored conductive layer may be composed of well-known conductive carbon black, and aluminum foil or aluminized layer can also be utilized.

DETAILED DESCRIPTION OF THE INVENTION

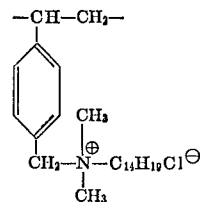
The following examples serve to illustrate the invention in more detail although the invention is not limited to the examples. Unless otherwise indicated, the amounts of the component are designated by parts by weight.

Example 1

A paper web comprising 50 parts of bleached hardwood kraft pulp, 50 parts of bleached softwood kraft pulp, 0.5 parts of rosin and 2.5 parts of alum, and weighing 60 grams per square meter was prepared. The paper web was coated with a coating composition containing 45 parts of conductive carbon black, 115 parts of alkyl resin modified by styrene and 145 parts of toluol. Coated weight was 5 grams per square meter on dry basis. The degree of electrical resistance of the resultant conductive coated paper sheet was 150 ohms per square.

On the other hand, four kinds of coating composition as shown in Table 1 were prepared using a copolymer

comprising 70 mol percent of styrene and 30 mol percent of monomer having following chemical structure:



The mean molecular weight of the copolymer was about 8,000. The copolymer is referred to as Copolymer A in the Table 1.

These coating compositions were then applied by coating rod onto the carbon coated papers by 10 grams per square meter on dry basis, respectively.

TABLE 1

Components, parts	Run 1	Run 2	Run 3	Run 4	Control
Zinc oxide.....	70	70	70	70	70
Titanium dioxide.....	30	30	30	30	30
Ethylcellulose.....	20	20	20	20	20
Copolymer A.....	5	10	15	20	0
Ethyl alcohol.....	306	312	324	336	348
Toluene.....	204	208	216	224	232

The recording sheets of Table 1 were placed in facsimile recorder having the stylus connected to the power source of 30K ohm impedance.

The Table 2 shows the power consumption of each sample required for reaching the reflection density of 1.0 scanned with 6 lines per millimeter.

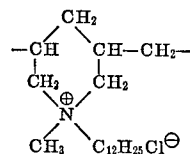
TABLE 2

	Power consumption (watt)
Run 1	3.8
Run 2	2.4
Run 3	1.8
Run 4	1.4
Control	4.8

Recording blanks in accordance with the preferred procedure given above are of low power consumption with less dust and less odor and better durability of stylus and shown uniform black on white trace and tone graduation.

EXAMPLE 2

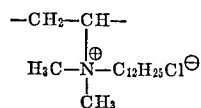
This example was similar to Example 1 except that the polymer obtained by polymerizing a monomer having the following chemical structure was used instead of Copolymer A of Example 1. The mean molecular weight of this polymer was 5,000.



Satisfactory results similar to those reported in Example 1 were obtained by recording in the same way as Example 1.

EXAMPLE 3

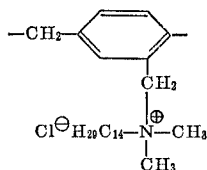
This example was similar to Example 1 except that the polymer obtained by polymerizing a monomer having the following chemical structure was used instead of Copolymer A of Example 1. The mean molecular weight of this polymer was about 8,000.



Satisfactory results similar to those reported in Example 1 were obtained by recording in the same way as Example 1.

5 EXAMPLE 4

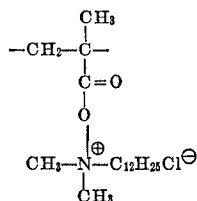
This example was similar to Example 1 except that the polymer obtained by polymerizing a monomer having the following chemical structure was used instead of Copolymer A of Example 1. The mean molecular weight of this polymer was about 20,000.



Satisfactory results similar to those reported in Example 1 were obtained by recording in the same way as Example 1.

Example 5

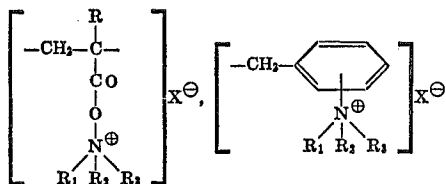
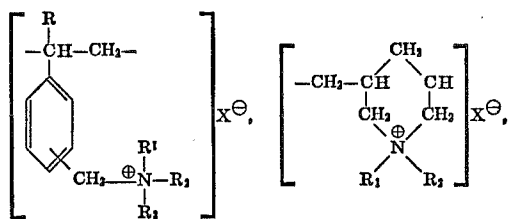
This example was similar to Example 1 except that the polymer obtained by polymerizing a monomer having the following chemical structure was used instead of Copolymer A of Example 1. The mean molecular weight of this polymer was about 5,000.



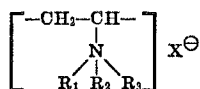
Satisfactory results similar to those reported in Example 1 were obtained by recording in the same way as Example 1.

What is claimed is:

1. An electro-sensitive recording blank comprising a backing layer having an electro-conductive dark-colored coating thereon and having on said electro-conductive dark-colored coating a white surface coating, said white surface coating essentially consisting of a white pigment, a binder and at least one polymer, said polymer essentially consisting of at least one monomer unit selected from the group consisting of the monomer units represented by the following structural formulas:



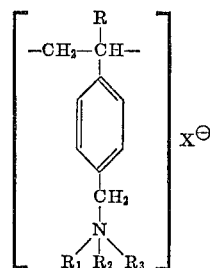
and



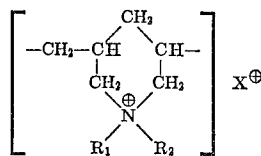
wherein R is hydrogen or alkyl having 1-4 carbon atoms, each of R₁, R₂ and R₃ is alkyl and at least one of R₁, R₂ and R₃ is alkyl having at least 10 carbon atoms, and X[⊖] is anionic radical.

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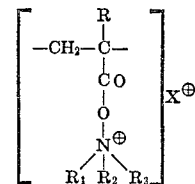
2. An electro-sensitive recording blank according to Claim 1 in which the polymer essentially consists of a monomer unit represented by the general formula:



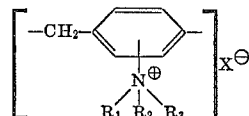
3. An electro-sensitive recording blank according to Claim 1 in which the polymer essentially consists of a monomer unit represented by the general formula:



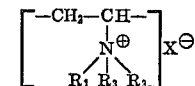
4. An electro-sensitive recording blank according to Claim 1 in which the polymer essentially consists of a monomer unit represented by the general formula:



5. An electro-sensitive recording blank according to Claim 1 in which the polymer essentially consists of a monomer unit represented by the general formula:



6. An electro-sensitive recording blank according to Claim 1 in which the polymer essentially consists of a monomer unit represented by the general formula:



7. An electro-sensitive recording blank according to Claim 1 in which the mean molecular weight of said polymer is within the range from 1,000 to 100,000.

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RALPH HUSACK, Primary Examiner

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,823,034

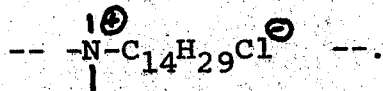
Dated July 9, 1974

Inventor(s) Taiji Higaki

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 20, correct to read $--CH_3SO_4^- --$.

Column 4, line 10, correct to read



Signed and sealed this 19th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

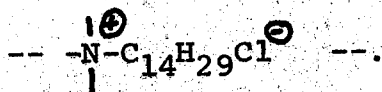
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