United States Patent [19]

Ferro

[11] **3,719,485**

[45] **March 6, 1973**

[54] **PHOTOCONDUCTIVE ELEMENTS INCLUDING BARRIER LAYER OF CONDUCTIVE OLIGOMERS**

[75] Inventor: **Anthony Ferro,** Middlebury, Conn.

[73] Assignee: **Uniroyal, Inc.,** New York, N.Y.

[22] Filed: **May 1, 1970**

[21] Appl. No.: **43,655**

Related U.S. Application Data

[62] Division of Ser. No. 679,956, Oct. 12, 1967, abandoned.

[52] **U.S. Cl.** .....**96/1.5,** 252/500, 260/80.3 S, 260/85.5 N, 117/201, 117/223, 162/138

[51] **Int. Cl.** **G03g 5/10,** G03g 5/02

[58] **Field of Search**.....260/465.4, 85.5 S, 80.3 N; 96/1.5; 252/500

[56] **References Cited**

UNITED STATES PATENTS

2,819,189	1/1958	Tzeng-Jiuegsuen	117/139.5
3,275,612	9/1966	Bechtold	260/88.7

Primary Examiner—George F. Lesmes
Assistant Examiner—M. B. Wittenberg
Attorney—Patrick Bright and Bert J. Lewen

[57] **ABSTRACT**

Coated articles, for example photoelectrostatic recording members, are made with a coating of an oligomer having the formula $H[CH_2CR'COOM]_a[CH_2CR^2X]_b - SO_3M'$ wherein M and M′ are water soluble cations; R′ and R^2 are hydrogen or methyl; X is a —CN or $—CONH_2$ group; $a + b$ is from 10 to 60 and $b/a + b$ is from 0.1 to 0.4 on a base.

5 Claims, No Drawings

PHOTOCONDUCTIVE ELEMENTS INCLUDING BARRIER LAYER OF CONDUCTIVE OLIGOMERS

This is a Division of Application Ser. No. 679,956, filed Oct. 12, 1967, now abandoned.

This invention relates to the use of bisulfite regulated oligomers as conductive agents, particularly to their use as conductive agents for the conductive barrier coating on photoelectrostatic copying paper or other photoelectrostatic recording members.

The conductive agent in the conductive barrier coating of the recording member in the photoelectrostatic copying process serves to give electrical conductivity to the non-metallic base - such as a sheet of paper — which has high electrical resistance.

Typically, the non-metallic base is coated on both sides with a conductive barrier coating. A photosensitive coating—composed of a photosensitive material, such as zinc oxide, a binder, such as an alkyd resin, and a sensitizing agent, such as an organic dye—is applied to one side of the base atop of the conductive barrier coating. This latter coating is composed of a conductive agent, usually in conjunction with tack reducing materials, such as pigments, waxes or polymers. If the base is porous, the two conductive barrier coatings may be connected.

In the photoelectrostatic copying process, the photosensitive coating layer is given a blanket negative charge in the dark, electrostatically, by passing a corona unit with a high negative voltage over the recording member. The material to be copied is then illuminated and, by mean of lenses and mirrors, its image projected onto the recording member's photosensitive surface. Where this image is white, light strikes the negatively charged photosensitive layer and causes this negative charge to drain off through the conductive barrier coating. Where this image is dark, no light strikes the negatively charged photosensitive layer and these areas remain charged.

There is now a laten electrostatic image on the recording member. To make this image visible and permanent, positively charged and colored particles, called toner particles, are brought in contact with the recording member. The toner particles may be dusted onto the recording member in powder form, as in the dry toner process, or in a solvent dispersion through which the recording member passes. The toner particles, being positively charged, adhere to those area of the recording member which have retained their negative charge and the latent image becomes visible. Where the charge has been drained off the recording member, the toner particles do not adhere to any appreciable degree.

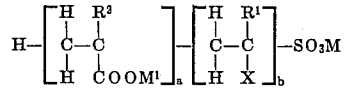
To make the reproduction permanent, the toner particles are fused to the recording member, by heating, if a dry toner process is used, or by air evaporation of the solvent, if a solvent dispersion of the toner is used.

The success of the photoelectrostatic copying process is dependent in several respects on the characteristics of the conductive agent. Most importantly, the conductive agent must be highly conductive over the broad range of temperature and humidity conditions at which copying machines are operated. This high conductivity permits the charge to drain quickly and completely from those areas of the conductive barrier coating where the light strikes and to produce sharp copies of the original and to prevent back marking and

reverse imaging. Naturally, also high condctivity is economically desirable; since satisfactory results may be obtained with the application of less material per unit area.

In preparing the recording member, it is desirable to have a solution or suspension of the conductive agent which has a low viscosity, particularly at high solids concentration, for ease of application and uniformity of coating. Other desired properties of the conductive agent are resistance to solvent, specifically in a solvent based copying process, in order to prevent solvent penetration of the recording member; neutral color so as not to prevent preparation copies from being white where desired; and ease of preparaion in an aqueous medium. This later attribute permits the use of the conductive agent directly and avoids the necessity of removing solvent.

In accordance with the instant invention it has been discovered that oligomers having the following general formula are particularly useful as conductive agents for the purpose heretofore discussed:



where M is a water soluble cation such as an alkali metal or ammonia M′ is an alkali meal or ammonium; R^1 and R^2 are hydrogen or methyl; X is a —CN or —$CONH_2$ group; a + b is from 10 to 60, preferably from 15 to 40; $b/a + b$ is 0.1 to 0.4, preferably from 0.15 to 0.35

The acid form of the above oligomers, i.e., where M′ is hydrogen, may be prepared by the reductive polymerization technique illustrated in U.S. Pat. No. 3,646,099 to Leland E. Dannals, entitled "Oligomers." The acid form of the oligomer is thereafter neutralized to form the water soluble conductive agents of the invention. A variety of alkaline materials which neutralize the acid oligomer and form a water soluble oligomer salt may be used. These include alkali metal and ammonium hydroxides and carbonates. Most preferable are salts of the alkali metals having an atomic number of 19 or more. As a practical matter, of these, potassium salts are most desirable.

The conductive barrier coating may be conveniently applied to the base by any of the conventional techniques known to those skilled in the art. Since the bisulfate regulated oligomers may be prepared in an aqueous solution and since the reaction goes to substantially complete conversion, the polymerizate, after neutralization, may be used directly as the coating solution. No intermediate processing, e.g., the removal of solvent or unreacted monomer, is necessary.

As noted previously pigments, waxes and polymer may be added to reduce the cost and/or the tackiness of the resulting coating. The following table shows the composition of typical coating solutions.

TABLE A

Component	Part by wt./100 Parts Oligomer
Pigments	0 to 200
Tack reducing agents	0 to 5

Polymers	0 to 400
Water	200 to 1,000

Generally, the total solids in the aqueous solution are between 10 and 60 percent by weight. Viscosities for such solutions are from 10 to 20,000 cps., a range which permits easy application of the coating to the base paper.

Extenders, such as other polymers and pigments, may be added to improve the properties of the coating and decrease its cost. Examples of pigments which may be used are clay, titanium dioxide, calcium carbonate, hydrated alumina and talc. Other polymers, both conductive and non-conductive, include carboxylated SBR latexes, acrylate latexes and water soluble polycationic polymers. Starch may also be added. Ammonium stearate, calcium stearate and carbowax are examples of tack reducing agents which may be added.

In order to illustrate more clearly the invention attention is directed to the following examples:

EXAMPLE I

A typical laboratory preparation of the acid of the oligomers is performed in a one-quart reactor which is fitted with an agitator, a liquid phase thermometer, a reflux condenser, an additional funnel, and a gas induction tube leading into the vapor phase. This ensemble is in a thermostated bath at 31.8°C.

Into the reactor are placed 3.12 g. $NaHSO_3$ (0.03 gFW), 159.8 g. water, 90.72 g. acrylic acid (1.26 moles), and 12.7 g. acrylonitrile (0.24 moles). The ratio of moles of monomer of gFW $NaHSO_3$ is 50, and the mole fraction of acrylic acid based on all monomers is 0.84. This oligomer ma be represented as H-(acrylonitrile)$_8$-(acrylic acid)$_{42}SO_3Na$.

Nitrogen is allowed to flow slowly (ca. 100 cc/ min.) into the reactor through the gas induction tube. When the contents of the flask reach 31.4° C., 0.25 ml. 1 percent aqueous $(NH_4)_2S_2O_8$ is added over about a three hour period through the addition funnel. The next morning, the weight of the clear reaction product is 269.2 g. It has 39.2 percent solids which indicates 99.0 percent conversion. Its viscosity is 7,700 cps.

EXAMPLE II

Following the laboratory procedure of Example I, $(NH_4)HSO_3$ is used as the initiator to prepare H-(acrylonitrile)$_{7.5}$ — (acrylic acid)$_{22.5}$ — SO_3NH_4. $(NH_4)_2S_2O_8$ is again used as the activator. The reaction goes to 95 percent conversion. The 100 percent conversion solids is 34.9 percent. The viscosity is 1010 cps. as compared to 1450 cps. for the corresponding oligomer prepared with a $NaHSO_3$ initiator. This is substantially the same.

EXAMPLE III

Other acid forms of the oligomers useful in the invention having the following formulas are prepared using 3.47 grams of $NaHSO_3$ as the initiator and 0.04 grams of $(NH_4)_2S_2O_8$ as the activator per mole of monomers. In all runs the conversion is over 98 percent. The viscosity of an aqueous solution having about 35 percent solids is shown:

TABLE I

Oligomer	Viscosity, Cps.
H-(Acrylonitrile)$_{5.5}$ (Acrylamide)$_{2.0}$— SOhd 3Na (Acrylic Acid)$_{22.5}$	1800
H-(Acrylamide)$_{7.5}$ (Acrylic acid)$_{22.5}$ — SO_3Na	1300

These two oligomers also have low viscosity.

EXAMPLE IV

This example shows the effect of storage on reaction product viscosity and also on the effect of the initiator action on viscosity. All reactions are over 95 percent conversion and the oligomers are H-(acrylonitrile)$_5$-(acrylic acid)$_{15}SO_3M$. The following table shows the results obtained:

TABLE II

Initiator HSO_3— Cation	Activator S_2O_8=	% Solid at 100% Conversion	Viscosity, cps., as made/after 3 weeks
Sodium	Ammonium	45%	3200/2950
Sodium	Ammonium	50%	7300/7300
Sodium	Potassium	50%	6080/-
Sodium	Ammonium	50%	3780/-
Potassium	Potassium	45%	1100/1150
Potassium	Potassium	50%	2300/2450

The effect of time on viscosity is particularly important, not only because of the handling problems, but also because of the need to maintain constant viscosity for ease of process control. The above table shows that the potassium initiator gave outstandingly low viscosities even at high solids levels and that the viscosity was substantially constant over the three week period.

EXAMPLE V

Using the general procedure in Example I, several other oligomers of the invention, of the type described by the general formula, H-(acrylonitrile)$_b$-(acrylic acid)$_a$ SO_3Na, are prepared. DO (degree of oligomerization), is given by $(a + b)$, but is calculated from moles of monomer/gFW of reducing initiator. In this work DO is varied from 16 to 60, the mole fraction of acrylic acid $b/(a + b)$, from 0.500 to 0.0 and the percent solids from 10 to 60 percent.

The effect of these variables on viscosity, expressed in centipoises, is illustrated in the following table:

TABLE 3

DO	%, solids	$b/a+b$ 0.333	0.250	0.167
16	35%		186 cps.	
20	35%	2 phase	296 cps.	378 cps.
	40%		3200 cps.	
	50%		7300 cps.	
30	35%	2 phase	1450 cps.	1120 cps.
40	10%		2 phase	
	30%		2 phase	
	35%		7500 cps.	9600 cps.
50	30%		2 phase	
	35%		2 phase	7700 cps.
	40%		30M cps.	12M cps.
	50%		40M cps.	
60	10%		2 phase	

The above data show the low viscosity is achieved particularly at $b(a + b)$ ratios at 0.250 or less and at DO's of 30 or less. It should be further noted, however, that low viscosities at low solids contents, e.g., 10 per-

cent, could be obtained even where the DO was 60. In each case where two phases formed, upon neutralization, a homogeneous solution was obtained.

EXAMPLE VI

This example describes the preparation of, H-(acrylonitrile)$_{10}$-(acrylic acid)$_{30}$—SO_3Na and its potassium salt in which almost all of the acrylic acid groups are neutralized with potassium hydroxide. A one gallon reactor fitted in a like manner to the quart reactor of Example I is charged with 1707 g. water, 265 g. acrylonitrile, 1080 g. acrylic acid, and 52 g. $NaHSO_3$. The reactor is placed in a water bath thermostated at 29.8° C. and a nitrogen stream flows through the vapor phase of the reactor. The initiator, 1 g. $(NH_4)_2S_2O_8$ in 68 g. water, is added slowly so that 10 g. of the solution are in the reactor after 4 hours. The temperature of the reactants rises to 41° C. The reaction stands overnight and has 44.9 percent solids and a viscosity of 74,000 cps. 33 percent Aqueous KOH solution is added to the reaction product in quantity sufficient to neutralize 95 percent of the acrylic acid present. This salt solution is without haze or tint, has 37.8 percent solids, 1300 cps. viscosity and 6.5 pH.

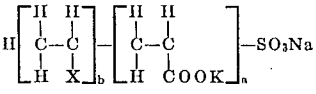
EXAMPLE VII

Using the procedure described in the previous example, except the oligomer H-(acrylonitrile)$_5$-(acrylic acid)$_{15}$—SO_3Na is prepared. The reaction product has 44.6 percent solids, and 4950 cps. viscosity and is clear and colorless. When enough 33 percent aqueous KOH to neutralize 95 percent of the acrylic acid is added to this reaction product, a salt solution of the oligomer is obtained. This is clear and colorless, has 37 percent solids, 230 cps. viscosity and 6.4 pH.

EXAMPLE VIII

As pointed out previously, the high conductivity of the conductive agent is a prime attribute particularly if this conductivity remains high over the range of temperature and humidity encountered under operating conditions.

To determine the conductivity of the oligomer both sides of a base stock are coated with various aqueous solutions of oligomer so that two pounds are coated per each 3,000 square feet. The surface resistance of the coating is measured with Kiethly conductivity apparatus at a 100 volt electrode potential. The oligomers tested have the formula:



The table indicates the values of X, $a + b$, $a/a + b$, and the specific resistance in megohms at 10 percent and 50 percent relative humidity (before and after the slash mark, respectively):

TABLE 4

X	Acrylonitrile				Acryl amide
b/a + b	0.5	0.25	0.16	0.0	0.25
a + b					
16	24,000/11	2000/23			
20				270/9.5	680/14
40		110/7.9		120/16	240/11
50		280/8.3			
60		150/16		73/8.8	

The above data clearly show the low resistivity of the coatings prepared in accordance with the invention. For comparison a typical commercial conductive agent has a specific resistance of 1500 megohms at 10 % percent relative humidity and 76 megohms at 50 percent relative humidity, figures clearly inferior to the preferred conductive coating agents of the invention.

EXAMPLE IX

This example illustrates the effect of the cationic group on the conductivity of the dried oligomer film. The acid form of the oligomer, having the formula: $N(CH_2CHCOOH)_{152}CHCN)_5SO_3Na$, are neutralized with the alkali metal and ammonium hydroxides to a pH of 7.5 and coated on a West Virginia rosin sized electrofax base stock. The sheets are cut up, conditioned at the desired relative humidities and resistivity readings taken. The results are shown in the following table:

TABLE 5

Coating	Total Coat Wt. (No./3000 Ft.^{2})	Surface Resistivity (Megohms/Sq.) 20% R.H.	50% R.H.
Li	3.9	1,600,000	33,000
NH_4	2.7	1,100,000	28,000
Na	3.8	7,200	310
K	3.6	300	20
Rb	4.8	140	16
Cs	3.7	92	31

The above data clearly show that the larger cationic groups are most advantageous. From the commercial standpoint potassium is clearly most preferable (because of its availability), since no appreciable improvement is obtained with the larger cations.

EXAMPLE X

Samples of paper coated with $H(CH_2CHCOOK)_{15}(CH_2CHCN)_{5cn}SO_3Na$ were heat-aged for 96 hours at 100° C. There was only a very slight discoloration. Similar sheets were light-aged in the Fadeometer for 96 hours with little or no discoloration.

The coated sheets with the zinc oxide photosensitive top coating were aged for 45 days at 72° F. and 50 percent relative humidity. These sheets imaged well using the laboratory SCM 33 copying machine. This indicates that there is no oligomer migration during storage of the sheet.

Films of this oligomer have been aged at 72° F. and 50 percent relative humidity for 5 weeks with no apparent migration within the film or any detrimental effects to the film. Additionally, the film has good solvent resistance to mineral spirits and toluene and is odorless.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. A photoelectrostatic recording member which comprises (1) a non-metallic base sheet; (2) a conductive barrier coating containing an oligomer having the formula $H[CH_2CR'COOM]_a\ [CH_2CR^2X]_b—SO_3M'$ wherein M and M' are water soluble cations; R' and R^2 are hydrogen or methyl; X is a —CN or a $—CONH_2$ group; $a + b$ is from 10 to 60 and $b/a + b$ is from 0.1 to

0.4 coated upon at least one surface of said base sheet; and (3) a photoconductive or an electrically photosensitive coating on one of the conductive barrier coatings.

2. The photoelectrostatic recording member of claim 1 wherein M and M′ are alkali metal or ammonium groups; R^1 and R^2 are hydrogen; and $a + b$ is from 15 to 30.

3. The photoelectrostatic recording member of claim 1 wherein X is —CN.

4. The photoelectrostatic recording member of claim 1 wherein X is $-CONH_2$.

5. The photoelectrostatic recording member of claim 1 wherein said sheet is paper.

* * * * *