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[54] **CONTINUOUS TONE ZNO - ACRYLIC POLYMER BINDER AND ADDITIVE**

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Related U.S. Application Data

[63] Continuation of Ser. No. 63,933, Aug. 14, 1970, abandoned.

[52] **U.S. Cl.** **96/1.8;** 96/1.5; 96/1.7

[51] **Int. Cl.²** **G03G 5/08**

[58] **Field of Search** 96/1.5, 1.7, 1.8

[56] **References Cited**

UNITED STATES PATENTS

3,347,670 10/1967 Nelson et al. 96/1.5

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[57] **ABSTRACT**

Electrophotographic continuous tone reproduction sheet in which the coating composition therefor includes continuous tone zinc oxide pigments, an insulating polymer resin binder selected to provide uniform optical density of the finished product, and in addition preferably includes an additive to enhance the optical density properties of the finished product.

8 Claims, No Drawings

CONTINUOUS TONE ZNO - ACRYLIC POLYMER BINDER AND ADDITIVE

This is a continuation of application Ser. No. 63,933, filed on Aug. 14, 1970, now abandoned.

FIELD OF INVENTION

The present invention relates to electrophotographic reproduction sheets and/or to electrophotographic coating compositions and more particularly to sheets and coating compositions capable of producing continuous tone prints of photographic quality from an original.

BACKGROUND OF THE INVENTION

Conventional silver halide technology is the method most used today for reproducing and enlarging pictures and transparencies. Although usual photographic techniques produce good quality prints of originals, the expense involved and the time required to produce a copy are major disadvantages.

Over the years attempts have been made at utilizing electrophotographic, electrostatic or electrofax techniques to reproduce pictures and transparencies. Although somewhat satisfactory results have been obtained, systems utilizing such techniques have not become widely utilized primarily because the quality of the reproduction was not generally as high as could be achieved using standard photographic reproduction procedures.

Generally these systems suffered from prints that lacked uniform optical density, i.e. smoothness and fill-in across a predetermined area, in each step of the usual gray scale. Thus, in prints produced by these techniques, large variations in grayness would appear in an area which should have been one continuous tone.

In addition, the prints of the prior art were usually limited to four to seven steps or graduations on a 21 step photographic gray scale of 0.15 (O.D.) increments optical density. For photographic quality prints, it has been found that about 15 or more steps are necessary to provide prints which are competitive with those produced using silver halide photoreproduction chemicals and techniques.

THE INVENTION REDUCES THE PRIOR ART DISADVANTAGES

The present invention provides an electrophotographic sheet and coating composition which can provide prints having about 15 or more steps (latitude) on a 21 step gray scale and a very small drop-off variation in optical density and therefore good smoothness and fill-in across a predetermined area.

BRIEF DESCRIPTION OF THE INVENTION

In order to provide the improved electrophotographic sheet as well as the coating therefor suitable for use in continuous tone electrophotograhic applications, a coating is formed which contains what is known in the trade as continuous tone zinc oxide pigments.

Continuous tone electrophotograhic zinc oxide pigments are generally white, readily accept dye sensitizers and are particularly useful to reproduce various tones or shades of gray. This type of zinc oxide pigments can, for example, be purchased from the New Jersey Zinc Company, of New York, N.Y., as either grade CT-011 of CT-012.

The coating also contains as insulating binder for the pigments. In continuous tone applications it has been found that the insulating binder composition utilized in the coating should have electrical properties which will provide good optical density as well as a broad latitude (number of distinct degrees or steps of grayness).

Various resin systems have been tested, but to date the best and most preferred binder resins uncovered are the acrylic polymer resins having properties suitable for electrophotographic applications. The most outstanding acrylic polymer binders uncovered to date are the styrene-acrylate resins and more particularly such polymers having repeating styrene and ethyl acrylate as units. A polymer of this class may be purchased from Desoto, Inc. of Des Planes, Illinois, U.S.A. under the designation Desoto E-048. In addition to the above, it has been found that the alkyd resins suitable for electrophotographic applications may also be utilized as the binder, but these are less preferred since they give somewhat poorer density, latitude and smoothness of print. An alkyd resin suitable for such purposes may be obtained from the aforementioned Desoto, Inc. as Desota E09. It has also been found that a combination or mixture of both alkyd and acrylic polymer resins may be utilized although again not providing properties equal to the acrylic polymer resin itself. Such resins as, for example, the Desoto resins E09 and E048 may be combined in a 1:1 ratio or may be combined in any other ratio as, for example, 1:10 or 10 to 1.

The aforementioned resin, including the Desoto resins, are generally sold as a solution e.g., in toluene having about 50% solids by weight, although obviously the percentage solids can vary.

It has been found in practice for continuous tone electrophotographic applications the pigment to binder solid ratio by weight should be between 9 to 1 and 3 to 1, between 7 to 1 and 4 to 1 being preferred, and a ratio of 5 parts pigment to 1 part binder resin solids by weight being most preferred. It has been found in practice that when the ratio exceeds about 9 to 1, adhesion of the coating to the base paper of the sheet substantially decreases and in addition, the uniform optical density of the end product (print) substantially deteriorates. At ratios less than 3 to 1, it has been found that blotchiness and non smoothness begins to appear in the resulting product (print) to a degree where good quality reproduction is no longer achievable. It has also been found that for continuous tone applications the binder and pigments, when formed into a coating, should have a saturation voltage between 300 to 100 volts and most preferably between about 250 to 150 volts. It has also been found to provide optimum continuous tone reproduction that the coating should exhibit substantially a linear charge voltage decay in the presence of light. Coatings used in normal electrophotography generally exhibit a non-linear decay. Substantially linear light decay has been accomplished in this invention by using the aforementioned coating formulations.

The coating herein is mixed and processed using conventional techniques and is then applied to a electrophotographic base paper such as Weyerhauser Paper Company, sold under the designation of CC Base. K.

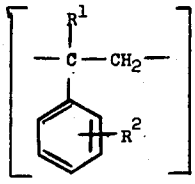
It has been found in practice that for continuous tone applications the paper should preferably weigh about 35 to 90 lbs./3000 square feet ream, and preferably be about 2 to 4 mils thick, but it should be understood that

this is not critical and can vary over a wide range depending upon the applications.

In continuous tone applications, it has been found that the coating weight (binder + pigment) should preferably be between 12 to 25 lbs. per 3000 square feet of paper and most preferably between 14 to 20 lbs. per 3000 square feet of paper.

In addition, it is preferable that the coating have a thickness of 0.4 to 0.8 mils, and most preferably a thickness of 0.5 to 0.7 mils.

As another important feature of this invention, it has been found in practice that the optical properties, in particular the uniform optical density of the finished print is enhanced by the use of a polymer (resin) additive. The preferred class of polymer resin additives have the repeating unit



where R^1 is lower alkyl or hydrogen, R^2 is lower alkyl or hydrogen and where the above lower alkyl has 1 to 4 carbon atoms (i.e. methyl, ethyl, propyl, butyl). Most preferably R^1 or R^2 is methyl and most preferably one is methyl while the other is hydrogen.

In practice it has been found that the polymer resin poly-α-methyl styrene, such as sold by Dow of Midland, Michigan, provides the best results as a resin additive although poly-vinyl toluene resins, that is where R^2 is ortho, meta, or para methyl and R^1 is hydrogen, may also be used. For continuous tone electrophotographic applications it has been found that additive should be employed such that the amount thereof is 5 to 40% by weight of the solid binder. More preferably the amount of additive should be 10 to 30% of the weight of the binder solids and most preferably 10 to 15% of the weight of the binder solids.

As in most conventional electrophotographic coatings, the coating preferably includes sensitizing dyes to achieve wider spectral response. Various sensitizers well known in the art may be used, as for example, those disclosed in U.S. Pat. No. 3,469,979, as well as those disclosed in the Examples herein.

After the sheet is formed it is utilized in a conventional electrophotographic copier, such as that sold by Dennison Manufacturing Company, Framingham, Mass. as the Dennison Standard Copier, except that the machine is modified so that the sheet is permitted to undergo saturation or near saturation development. This is accomplished by slowing the movement of the sheet through the toner used to develop the sheet. It has been found that this can be accomplished by permitting an immersion time in the toner to 15 seconds although this can vary depending on the toner and concentration thereof used. Well known toners which are usable include those manufactured by Hunt Chemical Corp., Interchemical, and Bell and Howell, among others.

In use the electrophotographic sheet of this invention is passed through the copier such that it is first charged using corona charging until it reaches maximum charge acceptance, generally 1 to 2 seconds being sufficient, is then exposed to light and then is permitted to undergo saturation or near saturation development. Thereafter, the print is dryed in a conventional manner. Photoreproduction sheets made in accordance with this invention were used in the Dennison Standard Copier as modified above and prints of photographs were made and were of good quality approximately that of the original in tone and latitude.

DETAILED DESCRIPTION

EXAMPLE 1

Mix 20 gms. of Desoto E 048 (which is a mixture of 50% solids in toluene) styrene ethyl acrylate resin binder with 45 gms. of toluene solvent. Then mix into it 3 gms. of Dow 276-V2 poly alpha methyl styrene. Add 50 gms. of New Jersey Zinc Continuous Tone ZnO CT-012 together with 0.75 ml of sensitizing dye solution (prepared by mixing 0.029 grams bromophenol blue, 0.59 grams uramine (USP), 0.135 grams methylene blue dissolved in 99 grams methanol) into the solution. After a homogeneous solution is obtained by vigorous stirring it is passed through a colloid mill in order to get a more uniform mix and to break down the particulate agglomerates. A Hegman gauge reading of about 5 is preferably obtained.

The mix is then placed on a sheet of electrofax base paper 2 mls thick, weight 40 lbs/3000 sq. ft. and a draw down using a wire wound Mayer rod is made. The sheet is coated with the composition such that the coating is 0.6 mls thick. The coated sheet is then dried in an oven at 110°F for 2 minutes to drive out excess solvent and then the sample is preferably placed in a dark black bag for dark conditioning for several hours. The sample is now ready to be used.

EXAMPLES 2 – 10

Using the method of Example 1, the following coating compositions were prepared and then applied to the base paper.

Example	Toluene Solvent	Dow 276-V2	Desoto EO-48	ZnO (CT-012)	Dye Solution (Formulation as Example 1)
2	45 gm.	—	20 gm.	50 gm.	.75 ml
3	45 gm.	.5 gm.	20 gm.	50 gm.	.75 ml
4	45 gm.	1 gm.	20 gm.	50 gm.	.75 ml
5	45 gm.	5 gm.	20 gm.	50 gm.	.75 ml
6	45 gm.	1 gm.	20 gm.	50 gm.	.75 ml
7	47 gm.	1 gm.	25 gm.	50 gm.	1.0 ml
8	50 gm.	1 gm.	33.4 gm.	50 gm.	1.25 ml
9	40 gm.	1 gm.	14 gm.	50 gm.	.25 ml
10	45 gm.	1 gm.	11.2 gm.	50 gm.	.25 ml

EXAMPLES 11 - 20

Using the method of Examples 1–10, modified compositions of those set forth in Examples 1–10 are prepared using the same amount and preparations of ingredients, except that continuous tone New Jersey Zinc Oxide CT-011 is substituted for New Jersey Zinc Oxide CT-012.

EXAMPLES 21 - 40

Using the method of Examples 1–20, modified compositions of those set forth in Examples 1–20 are prepared using the same amount and proportions of ingredients except that the dye used was a Rose Bengal 0.5 grams and Bromophenol Blue 0.5 grams in 99 grams of Methyl Cellusolve.

EXAMPLE 41

Using the method of Example 1, a coating composition is prepared by mixing the following ingredients; toluene 45 gm., Dow G257 3 gm., Desoto E-09 alkyd resin 11.5 gm., New Jersey Zinc Oxide CT-102 50 gm.

EXAMPLE 42

Example 41 is repeated except that 0.75 ml of the dye of Example 1 is added thereto.

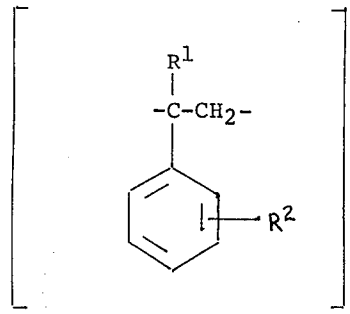
EXAMPLE 43

Using the method of Example 1, a modified coating composition is prepared by using 20 grams of a 1:1 blend of Desoto resin E048 and E09.

The above description and examples are for illustrative purposes only and it is not intended that the invention be limited thereto, but only to the products claimed in the claims appendant hereto.

We claim:

1. An electrophotographic reproduction sheet having an electrophotographic coating consisting essentially of continuous tone zinc oxide pigment providing about 15 or more steps on a 21-step photographic gray scale of 0.15 (O.D.) increments, an insulating acrylic polymer binder therefor and a polymer resin additive having the repeating unit



where

R^1 is lower alkyl or hydrogen,

R^2 is lower alkyl or hydrogen, and

wherein said lower alkyl has 1 to 4 carbon atoms, positioned on a base paper, said pigment and binder having a ratio by weight in the range from about 9:1 to about 3:1, and said additive being present in an amount which is in the range from about 5 to 40 percent of said polymer binder.

2. A sheet according to claim **1** where R^1 is CH_3 and R^2 is hydrogen.

3. A sheet according to claim **1** where R^1 is hydrogen and R^2 is CH_3 at the ortho, meta or para position of the phenyl ring.

4. A sheet according to claim **1** in which the resin additive is 10 to 30% by weight of the polymer binder solids.

5. A sheet according to claim **1** in which the polymer binder is a styrene-acrylate resin.

6. A sheet according to claim **1** in which the polymer binder is a styrene ethyl acrylate resin.

7. An electrophotographic sheet according to claim **1** in which the base paper has a weight of 35 to 90 lbs. per 3000 sq. ft. ream and wherein the coating is applied at a weight between 12 to 25 lbs. per 3000 sq. ft. ream.

8. An electrophotographic sheet according to claim **1** in which the coating contains a sensitizing dye.

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