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3,485,624
PHOTOCONDUCTIVE PROPERTIES OF
POLY-N-VINYL CARBAZOLE

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2 Claims

ABSTRACT OF THE DISCLOSURE

According to the present invention, a substantial in-
crease in photographic speed of photoconductive coat-
ings containing poly-N-vinyl carbazole is obtained by
heat treatment of such coatings at a temperature in the
range from about 250° C. to about 300° C. for a time
period from about 15 minutes to about 1 hour.

This invention relates to electrophotography. More
particularly, the invention relates to electrophotographic
elements comprising a photoconductive insulating coat-
ing on a support.

Poly-N-vinyl carbazole is a compound used for its
photoconductive properties in certain reproduction pro-
cesses which utilize electrostatic charges. Use of poly-N-
vinyl carbazole as an organic photoconductor in electro-
photographic elements is described in numerous litera-
ture references, for example, in U.S. Patent No. 3,037,861,
patented June 5, 1962.

An object of the invention is to provide improved elec-
trophotographic elements comprising an annealed photo-
conductive coating containing the organic photocon-
ductor, poly-N-vinyl carbazole.

Another object of the invention is to provide a method
for improving the photographic speed of photoconductive
electrically insulating coatings containing the organic
photoconductor, poly-N-vinyl carbazole.

According to the present invention, a substantial in-
crease in photographic speed of photoconductive coatings
containing poly-N-vinyl carbazole is obtained by heat
treatment of such coatings at a temperature in the range
from about 250° C. to about 300° C. for a time in the
range from about 15 minutes to about 1 hour. The higher
the temperature, the shorter the time. At temperatures
lower than 250° C., the effect is negligible, whereas at
temperatures above 300° C. the degradation of the
polymer is too important for it to be used in a photo-
conductive coating.

It has also been found that much more sensitive photo-
conductive coatings were obtained when crystalline poly-
N-vinyl carbazole was used instead of the amorphous
polymer. By comparison with the amorphous poly-N-vinyl
carbazole, the crystalline polymer shows a $T_{1/10}$ period,
such as defined hereunder, which is more than twice
smaller (about 6 to 8 seconds instead of 17 to 20 seconds)
and the practical exposure time, which is also defined
hereunder, is divided by a still greater factor (4 to 5
seconds instead of 12 to 30 seconds).

In this specification, the $T_{1/10}$ period is the time re-
quired for the potential of a photoconductive layer to
reach $\frac{1}{10}$ of the value of the potential after the initial
charge, when said layer is subjected to an illumination of
13,600 lx. The practical exposure time is the minimum
exposure time in seconds, under the same 13,600 lx.
illumination, required to obtain the best possible image
without any background fog, with magnetic brush de-
velopment. Thus the lowest number indicates the highest
photographic speed.

The heat treatment may be conducted as well on coat-
ings comprising either commercial amorphous poly-N-
vinyl carbazole or on crystalline poly-N-vinyl carbazole.
Examples of commercial amorphous poly-N-vinyl carba-
zole are Luvican M-170 or M-710 sold by Badische
Anilin Soda Fabrik. Crystalline polymers with which
we experimented were synthesized in our laboratory by
the process described in Belgian Patent No. 606,790.
With both amorphous and crystalline samples, the results
obtained by heat treatment were quite similar. We prefer
the crystalline materials because they provide better re-
sistance to degradation by heating. With both types,
however, at the annealing temperatures used, heat de-
gradation was slight enough to be tolerable.

The following examples are provided to describe cer-
tain preferred embodiments of the invention.

EXAMPLE 1

A solution of poly-N-vinyl carbazole in benzene is
prepared by dissolving 6 gm. Luvican M-170 in 100 ml.
benzene. The solution is coated on an aluminum plate
and the solvent is evaporated at room temperature in
air, leaving a film of poly-N-vinyl carbazole coated on
the metal support. The coating is electrically insulating
and photoconductive. The coated plate is placed in an
electric oven in a nitrogen atmosphere and heated to
annealing temperature; the sample is annealed for a period
in the range from about 15 minutes to about 1 hour. In
Table 1 are tabulated descriptions of test results obtained
with samples prepared as described above and annealed
for the times and at the temperatures shown in the table.

TABLE 1

Heat treatment	Coating thickness in microns	Initial potential (volts)	Reduction of charge in darkness, 3 minutes (percent reduction)	$T_{1/10}$	Practical exposure time (seconds)
None	10	800	10	1.7	30
15 min., 250° C.	10	1,000	33	1.7	2
60 min., 250° C.	8	650	30	1.4	2
15 min., 275° C.	8	600	19	3.7	5
60 min., 275° C.	6	490	28	1.1	1.4
15 min., 300° C.	9	800	24	1.4	1.4

The test results tabulated in Table 1 were obtained by first dark-adapting each plate for several days and then applying an electrostatic charge by means of corona discharge. The natural charge decay after 3 minutes was observed and recorded. The $T_{1/10}$ period and the practical exposure time, such as defined above, were also observed and recorded.

EXAMPLE 2

The procedure of Example 1 was repeated, except that the coating solvent used was a 53/33/14 mixture of benzene, methylene chloride and dioxane, with poly-N-vinyl carbazole prepared by the process described in the aforesaid Belgian Patent No. 606,790. In Table 2 are tabulated tests results obtained as in Example 1.

TABLE 2

Heat treatment	Coating thickness in microns	Initial potential (volts)	Reduction of charge in darkness, 3 minutes (percent reduction)	$T_{1/10}$	Practical exposure time (seconds)
None	13	1,200	12	6-8	4
60 min., 250° C.	10	1,200	40	0.4	—
180 min., 250° C.	10	1,000	74	0.1	—
480 min., 250° C.	8	1,200	43	0.1,	—
180 min., 275° C.	10	550	78	0.3	—
180 min., 275° C.	10	950	85	0.2	—
180 min., 300° C.	13	1,000	61	0.4	—
60 min., 330° C.	12	210	65	3.5	—

In the last column of Table 2, the sign (—) indicates that the practical exposure time is too small to be measured.

In describing certain preferred embodiments of our invention, we have used coatings consisting essentially of poly-N-vinyl carbazole. However, our invention extends to use of the improvements with poly-N-vinyl carbazole in electrophotographic photoconductive coatings which may also contain other organic polymers in combination with poly-N-vinyl carbazole. Such coatings are described in the literature. Our invention further extends to use of the improvements with photoconductive coatings containing photoconductive poly-N-vinyl carbazole with added sensitizers, activators, and the like, of various kinds known and used in the arts relating to organic photoconductive coatings.

It will be understood that modifications and variations

may be made within the scope of the invention as described above and as defined in the following claims.

We claim:

1. A method for improving the photographic speed of electrophotographic elements comprising a support and coated thereon a photoconductive electrically insulating layer comprising photoconductive poly-N-vinyl carbazole, said method comprising the step of annealing said electrophotographic element at a temperature in the range from 250–300° C. for a time in the range from 15 minutes to 1 hour.

2. An improved electrophotographic element for use in electrophotography comprising a support and coated thereon an annealed, electrically insulating photoconduc-

tive coating comprising photoconductive poly-N-vinyl carbazole, said element having been heat-annealed at a temperature in the range from 250–300° C. for a time in the range from about 15 minutes to about 1 hour.

References Cited

UNITED STATES PATENTS

2,863,767 12/1958 Vyverberg et al. 96—1
3,037,861 6/1962 Hoegl et al. 96—1.5
3,421,891 1/1969 Inami et al. 96—1.6

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