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[54]	HEAT-SENSITIVE COPY-SHEET	3,293,061 12/1966 Lawton117/36.8	
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[73]	Assignee: Minnesota Mining and Manufacturing Company, St. Paul, Minn.	3,483,013 12/1969 Berg et al. 117/36.2 3,573,958 6/1971 Small. 117/36.8 3,594,208 7/1971 Wiese et al. 117/36.9	
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[21]	Appl. No.: 90,120	Primary Examiner—Murray Katz Attorney—Kinney, Alexander, Sell, Steldt & Delahunt	
[52]	U.S. Cl117/36.8, 117/138.8 F, 117/155 UA	[57] ABSTRACT	
[51] [58]	Int. Cl. B41m 5/22 Field of Search 117/36.9, 36.8, 36.2	A coating composition containing a dye, such for example as Genacryl Orange, and tetramethylguanidine trichloroacetate	
[56]	References Cited	in a solution of inert binder at a pH not higher than 3 is applied to a carrier sheet to form a colored coating which on brief	
	UNITED STATES PATENTS	standing becomes colorless and heat-sensitive.	
3,166	,583 1/1965 Martin et al117/36.8	4 Claims, No Drawings	

HEAT-SENSITIVE COPY-SHEET

This invention relates to heat-sensitive copy-sheet materials useful in the reproduction of graphic originals by the thermographic copying process involving brief exposure of the original to intense radiation while in heat-conductive contact with the copy-sheet. In one important aspect the invention relates to a novel method of making the copy-sheet. In another aspect the invention relates to clear transparent copy-sheet materials from which color projection transparencies may be thermographically prepared.

The copy-sheets of this invention are prepared from solutions containing a suitable dye as hereinafter defined together with tetramethylguanidine trichloroacetate and with sufficient trichloroacetic acid to provide a pH not higher than 3. An inert binder is included and the solution is coated on a suitable carrier or may be dried as a thin film on a temporary support and then stripped therefrom for use in absence of a carrier. Paper carriers are useful but clear transparent films, particularly heat-resistant films such as Mylar polyester films, are preferred. Polyvinyl acetate is a preferred example of an inert polymeric film-forming binder.

The following dyes have been found particularly effective in copy-sheets made in accordance with this invention:

Genacryl Blue 66-G.F.	(CI 42025)
Genacryl Orange G	(CI 48035)
Genacryl Yellow 5GF	(CI 48065)
Genacryl Yellow 3G	(CI 48055)
Genacryl Red 6B	(CI 48020)
Genacryl Orange R	(CI 48040)

The tetramethylguanidinium trichloroacetate, and sufficient trichloroacetic acid to give the required pH, are dissolved together in a minimum quantity of water and the solution is then added to a solution of the dye and binder in a water-miscible organic solvent. The colored mixture is spread and dried, forming a colored dry film. Upon standing under normal room conditions for not longer than 24 hours, or in shorter times at moderately elevated temperatures, the film is found to be decolorized. It may then be made to become brilliantly colored by localized heating in the thermographic copying process. The thus developed images are permanent and project a colored image against a white background when the film is used as a projection transparency.

Surprisingly, all attempts to decolorize the solution prior to 45 coating and drying, e.g., by heating or by prolonged storage, result in a film product which remains colored on prolonged

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storage and therefore is not subsequently capable of forming a useful contrasty colored image by thermographic copying methods.

In a specific Example, 0.050 gm. of tetramethyl-guanidini5 um trichloroacetate is dissolved in 0.1 ml. of water and approximately one-tenth drop of dilute aqueous trichloroacetic acid is added to bring the pH of the solution to 3 as determined with "p Hydrion" (pH 1-5) indicator paper. Separately, 0.075 gm. of Genacryl Red 6B (CI 48020) is mixed with 5 gm. of a 10 percent solution of "Gelva V-100" polyvinyl acetate in methylethyl ketone. The acidified salt solution is mixed into the dye and binder solution and the mixture is coated on two mil Mylar polyester film using a coating orifice of three mils, and allowed to dry. The coated film is magenta colored. It fades and becomes colorless within less than 24 hours, or may be decolorized by moderate heating for much shorter periods.

The film as initially produced and while still colored is passed through a thermographic copying machine in contact with a graphic original. The image areas become colored an intense but still transparent magenta; the background areas become colorless. The clear film obtained after 24 hours storage produces a similar copy.

The amount of dye in the above formula may be reduced to as little as 0.005 gm. while still obtaining a projectable color image, and may be increased to as much as 0.5 gm. without causing the colorless coating to become light-diffusing. Within these ranges the amount of salt may also be varied so long as sufficient salt is present to cause conversion to the colored 30 image while still avoiding light-diffusion.

What is claimed is as follows:

- 1. A heat-sensitive copy-sheet comprising a colorless dry film residue of a colored solution in a water-miscible volatile organic solvent of (a) an aqueous solution of tetramethylguanidinium trichloroacetate containing sufficient trichloracetic acid to provide a pH not higher than 3, (b) an inert film-forming binder, and (c) at least one dye from the class of Genacryl Blue 6G-GF, Genacryl Orange G, Genacryl Yellow 5GF, Genacryl Yellow 3G, Genacryl Red 6B and Genacryl Orange R.
 - 2. Copy-sheet of claim 1 wherein the ratio of dye to tetramethylguanidinium trichloroacetate is about 3:2.
 - 3. Copy-sheet of claim 2 wherein the dye is Genacryl Red 6B and the binder is polyvinyl acetate.
- 4. Copy-sheet of claim 1 wherein the ratio of binder:dye:salt is about 20:3:2.

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