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Procedure for the Characterization of Zinc Oxide Photocopy Papers

ABSTRACT: A method is presented for the characterization of zinc oxide photocopy papers. The tests include nondestructive physical examinations of weight, pH, and color under ultraviolet light. Chemical tests, consisting of thin-layer chromatographic examination of the sensitizing dyes and infrared spectrophotometry of the binder resins, are carried out on extractions of the photoconductive surface layer. A semiqualitative flow chart has been prepared that permits differentiation of most of the zinc oxide photocopy papers on the basis of the composite of characteristics of 50 papers supplied by eleven manufacturers.

KEY WORDS: questioned documents, photocopiers, papers

Of the many methods devised for the reproduction of images, the method currently used with most commercially available copying machines is the electrostatic process, which uses the physical phenomena of electrostatics and photoconductivity.

Electrostatic attraction occurs when two appropriate objects are rubbed together, thus developing a charge capable of attracting small objects bearing an opposite charge.

Photoconductivity is the phenomenon by which certain substances exhibit greater conductivity in those areas exposed to light. A photoconductive surface, given a uniform electrostatic charge in the dark and subsequently imaged by light, will allow the charge in the lighted area to dissipate. Where no light has reached the surface, the charge remains, producing an electrostatic latent image. An oppositely charged powder applied to the surface will adhere only to those areas retaining the charge, thereby creating a visible image.

Two electrostatic processes used in document reproduction are xerography (transfer electrostatics) and Electrofax® (direct electrostatics). In xerography the image is formed on a selenium drum and transferred to a plain paper; however, in Electrofax the image is formed directly on a sheet of paper coated with a thin photoconductive layer of zinc oxide. The latent image is made visible by showering the paper surface with finely divided carbon particles of an opposite charge or by passing the paper through an organic solvent bearing charged carbon particles. The particles adhere to the sheet in the latent imaged areas to create the visible image.

This paper deals with a systematic procedure for the comparison of the chemical and

physical properties of the zinc oxide coated papers. The procedure involves nondestructive testing, consisting of color and weight determinations, and destructive testing, involving extraction and analysis of the photoconductive layer (resins and sensitizing dyes). Fifty different zinc oxide photocopy papers were contributed by eleven photocopy manufacturers. Each paper was identified by code. The testing was carried out on blank sheets as received from the manufacturer. The reagents and equipment used are listed in Table 1.

Weight Determination

The sample sheet is handled with rubber gloves and weighed to three decimal places on a single pan balance. The weights are converted to weight (in pounds) per 3000 ft^2 to coincide with paper manufacturers' specifications. The surface area of the paper is determined in square inches. The weight per 3000 ft^2 can be calculated with the following equation:

$$\text{weight (lb)}/3000 \text{ ft}^2 = 952.38 \times \frac{\text{weight (g)}}{\text{square inches of surface area}}$$

pH Test

The coated and base side of the sheet can be identified by visual examination or by scratching the surfaces with a sharp object. The sample is supported, base side up, on a

TABLE 1—*Reagents and equipment.*

Material	Description	Manufacturer/Supplier	Catalog Number
Balance	single pan, spring loaded, Model Zeta N-IV, Type 10 N	Wm. Ainsworth & Sons	1-920-110
pH solution	Universal Indicator Solution	Fisher Scientific	SO-I-60
pH chart	Universal Indicator Chart	Fisher Scientific	1-180
Disposable pipets	pasteur capillary, 145 mm (5¾ in.)	Sargent-Welch Scientific	S69647-KA
Vials	glass, 3.9 g (1 dram)	Kimble Products	60875-L
Thin-layer chromatography plates	SG60 precoated glass, silica gel without fluorescent indicator	Merck/E. M. Laboratories	5762
Disposable micropipets	1 μl	Drummond Scientific	7695-DO4
Disposable micropipets	micro-sampling pipets	Corning	7099-S
Centrifuge	International Equipment Co. micro-hematocrit, 11 500 rpm	Fisher Scientific	5-040
Solvents	reagent-grade methyl ethyl ketone; absolute ethanol; American Chemical Society grade methanol	...	...
Thin-layer chromatography solvent systems	chloroform (distilled in glass) and methanol, reagent grade (9:1)	...	...
Infrared spectrophotometer	Model 467, slit control-7, scan-mode-fast	Perkin-Elmer	990–9809
Ultraviolet light	long wave, 366 nm, Model XX15	Black Light Div. of Spectronics	...

TABLE 2—*The color and R$_f$ values*

Paper	Base Color Under 366-nm UV Light	Coating Color Under 366-nm UV Light	Weight, lb. per 3000 ft² (approximate)	Visual Band 1	Visual Band 2	Visual Band 3
pH 4.0 to 4.5						
Dennison V.Q.C. 09-608	Bl–BV	light purple	58	blue ring = 0	...	...
pH 5.0 to 5.5						
Mead Paper Co.	P–PV	purple	60	...	none	...
Dennison Hi-Speed 09-240	P–PV	purple	46	blue ring = 0	...	...
A.B. Dick 92-1600 XL	P–PV	pink	44	blue ring = 0	yellow = 12.0 (tailing)	...
A.B. Dick 92-1000	P–PV	pink	57	...	none	...
A.B. Dick 92-1300	P–PV	pink	58	blue ring = 0	yellow = 9.4	...
A.B. Dick 92-4500	P–PV	pink	53	blue ring = 0	yellow = 12.1	...
Addressograph Multigraph 32-157	P–PV	purple	57	blue ring = 0	yellow = 6.7	...
Addressograph Multigraph 32-156	P–PV	light purple	69	blue-brown ring = 0	yellow = 9.7	...
James River D	P–PV	pink	56	blue = 2.5	yellow = 22.5	...
James River B	P–PV	pink	56	blue = 0 (smearing)	yellow = 18.4	...
James River P	P–PV	pink	58	blue ring = 0	blue = 7.9	yellow = 21.0
James River F	P–PV	light pink	54	blue ring = 0	yellow = 18.3	...
James River R	P–PV	pink	53	blue ring = 0	yellow = 17.6	...
James River E-54	P–PV	purple	55	...	none	...
James River O	P–PV	purple	56	blue ring = 0	yellow = 18.4	...
Dennison Standard 09-200	Bl–BV	light purple	54	blue ring = 0	...	...
Dennison Hi-Speed 09-273	Bl–BV	pink	59	blue ring = 0	yellow = 10.5	...
Dennison Medium Speed 09-284	Bl–BV	pink	58	blue ring = 0	yellow = 8.6	...
Dennison Dielectric 09-198	Bl–BV	light purple	51	...	none	...
Nashua L-470	Bl–BV	light purple	58	blue ring = 0	...	...
Crown Zellerbach 963-03	Bl–BV	pink	55	blue ring = 0	...	...
3M Co.	Bl, Wh fl	pink	53	...	none	...
Dennison Copymaster 09-202	Bl, Wh fl	pink	49	blue ring = 0	...	...
Riegel H-0-18-16	P–PV	pink	60	faint yellow = 0	...	...
A.B. Dick 92-1200	Bl Wh fl	pink	62	...	none	...
Crown Zellerbach 583-13	Bl Wh fl	pink	56	...	none	...
Crown Zellerbach 501-02	Bl Wh fl	pink	56	blue ring = 0	yellow = 25.3	...
pH 6.0 to 6.5						
Riegel K-4-19-11	P–PV	light purple	56	...	none	...
Riegel K-3-25-15	P–PV	light purple	58	yellow = 0	...	...
Nashua L-302-26	P–PV	light purple	53	...	none	...
Nashua L-500	P–PV	pink	55	...	none	...
Addressograph Multigraph 83-1-100599	P–PV	purple	56	yellow = 9.8	...	...
Addressograph Multigraph 32-300	P–PV	purple	66	blue = 0	yellow = 6.7	...
Addressograph Multigraph 32-158	P–PV	pink	60	blue = 0	orange = 3.2	yellow = 9.7
Addressograph Multigraph 32-155	P–PV	light purple	70	blue-brown ring = 0	yellow = 9.4	...

of the visible and fluorescent bands.

R_f Value

		Under 366-nm UV Light					Spectrum Number
Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	Band 7	
pink = 0	yellow = 11.4	...	...	...	...	...	5
yellow = 0	...	...	...	...	...	...	4
pink = 0	yellow = 6.8	fluorescence = 93.2	...	...	...	...	11
fluorescence = 0	yellow = 11.3	...	...	...	...	...	8
yellow = 11.1	...	...	...	...	...	...	8
pink = 0	yellow = 9.4	pink = 21.9	...	...	...	...	8
yellow = 10.6 (tailing)	...	...	...	...	...	...	8
pink = 0	yellow = 6.7	...	...	...	...	...	4
pink = 0 (smearing)	yellow = 9.7	...	...	...	...	...	1
pink = 2.6	yellow = 23.1	...	...	...	...	...	4
pink = 0 (smearing)	yellow = 18.4	...	...	...	...	...	4
pink = 0	yellow = 21.0	...	...	...	...	...	8
yellow = 18.3	fluorescence = 90.1	...	...	...	...	...	4
pink = 0 (smearing)	yellow = 16.9	fluorescence = 94.4	...	...	...	...	8
white = 94.3	...	...	...	...	...	...	15
yellow = 18.4	white = 89.5	...	...	...	...	...	4
pink = 0	yellow = 5.4	...	...	...	...	...	5
pink = 0	yellow = 10.5	...	...	...	...	...	13
pink = 0	yellow = 8.6	...	...	...	...	...	13
...	...	...	none	...	...	...	9
yellow = 12.2	white = 70.3	fluorescence = 81.1	...	...	...	...	8
fluorescence = 0	blue-white = 67.6	blue-white = 73.5	...	...	...	...	8
yellow = 21.3	...	...	...	...	...	...	12
pink = 0	yellow = 4.3	...	...	...	...	...	5
yellow = 0	fluorescence = 76.3	...	...	...	...	...	3
yellow = 0	...	...	...	...	...	...	4
yellow = 8.8	...	...	...	...	...	...	8
fluorescence = 0	yellow = 25.3	...	...	...	...	...	16
...	...	...	none	...	...	...	3
yellow = 0	...	...	...	...	...	...	2
pink = 14.7 (tailing)	...	...	...	...	...	...	7
pink = 18.4	white = 72.4	fluorescence = 42.1 (faint)	fluorescence = 47.4 (faint)	fluorescence = 77.6 (faint)	...	...	7
pink = 0	pink = 3.3	yellow = 8.2	fluorescence = 41.0	blue-white = 65.6	blue-white = 73.8	...	7
yellow = 0	yellow = 6.7	pink = 16.7	...	...	...	...	4
pink = 0	orange = 3.2	yellow-green = 9.7	fluorescence = 21.0	fluorescence = 32.3	fluorescence = 54.8	fluorescence = 64.5	4
pink = 0 (smearing)	yellow = 7.8	...	...	...	...	...	1

TABLE 2—

Paper	Base Color Under 366-nm UV Light	Coating Color Under 366-nm UV Light	Weight, lb. per 3000 ft² (approximate)	Color and		
				Visual		
				Band 1	Band 2	Band 3
S.D. Warren 7100	P-PV	pink	62	...	none	...
S.D. Warren 6000	P-PV	pink	59	...	none	...
S.D. Warren 1100	Bl, Wh fl	pink	64	yellow = 0	blue-purple = 7.7	...
Dennison 09-511	Bl, Wh fl	light purple	59	...	none	...
Riegel J-9-14-7	Bl, Wh fl	light purple	57	yellow = 0	...	...
Riegel J-6-24-3	Bl, Wh fl	light purple	63	yellow = 0	...	...
Riegel K-4-1-20	Bl, Wh fl	purple	61	...	none	...
Riegel K-3-19-6	Bl, Wh fl	purple	64	yellow = 0	...	...
Riegel J-10-21-1	Bl, Wh fl	light purple	61	yellow = 0	...	...
A.B. Dick 92-1700	Bl, Wh fl	purple	60	...	none	...
pH 7.0 and up						
Nashua L-302	P-PV	light purple	55	...	none	...
Nashua L-302B	P-PV	light purple	55	...	none	...
Dennison 09-666	Bl, Wh fl	light purple	54	...	none	...
Pram Standard Speed	Bl, Wh fl	light purple	64	...	none	...
Pram High Speed	Bl, Wh fl	purple	63	...	none	...

clipboard positioned at an angle of about 60 deg. One drop of Fisher Universal Indicator Solution is applied to the base side of the sheet and allowed to flow down the sheet. The sheet is dried and the color of the stain is compared to the Fisher pH Universal Indicator Chart. The pH is recorded.

Ultraviolet Light Examination

The base side of the sheet is examined under long wavelength ultraviolet (UV) light (366 nm). Color and fluorescence are noted. These colors are categorized as either pink to pink violet (P-PV), blue to blue violet (Bl-BV) or blue, white fluorescence (Bl, Wh fl) and results recorded. The coated side of the sheet is examined under long wave UV light. The color is noted and this information is recorded as either pink, light purple, or purple.

Thin-Layer Chromatography of Sensitizing Dyes

With a razor blade or sharp object, the coating is scraped from a 25- by 25-mm (1- by 1-in.) area of the sheet. The coating is placed in a capped vial with three to four drops of ethanol to extract the dyes. The sample is allowed to stand about 15 to 20 h to insure extraction. Approximately 10 μl of the extract is spotted on the Merck SG60 thin-layer chromatographic (TLC) plate in 0.5-μl increments. Following each application, the sample is dried with a stream of warm air. The sample is applied approximately 25 mm (1 in.) from the end of the TLC plate by using a 1-μl disposable micropipet to minimize the diameter of the spot and thus insure optimum band resolution. The plates are identified and point of application is marked.

A TLC tank is prepared by using a chloroform/methanol (9:1) eluant and allowed to equilibrate. The TLC plate bearing the sample is placed in the equilibrated tank and

Continued.

R_f Value

	Under 366-nm UV Light						Spectrum Number
Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	Band 7	
pink = 2.6	pink = 10.5	pink = 15.8	fluorescence = 82.9	...	...	..	8
pink = 0	pink = 12.3 (tailing)	pink = 17.8	...	...	...	...	8
fluorescence = 77.9	...	...	...	...	...	...	4
pink = 0	pink = 5.4	...	...	...	...	...	5
yellow = 0	...	...	...	...	...	...	2
yellow = 0	...	...	...	...	...	...	2
...	...	...	none	...	...	...	3
...	...	...	none	...	... ...	...	2
pink = 0	fluorescence = 18.4 (tailing)	...	...	...	...	...	2
yellow = 12.5	fluorescence = 71.9	...	...	...	...	...	8
yellow = 14.7	yellow = 14.7 (tailing)	...	...	...	...	...	7
yellow = 21.3	...	...	...	...	...	...	8
pink = 0	yellow = 5.3	...	...	...	...	...	5
pink = 10.8	fluorescence = 91.9	...	...	...	...	...	8
pink = 9.5	...	...	...	...	...	...	8

allowed to develop for 8 min. On completion of the development, the TLC plate is removed, the solvent front is marked, and the plate is air-dried.

The chromatogram is examined under visible light and long wave UV light. The color and R_f values of the visible and the fluorescent bands are determined and recorded (Table 2). The R_f values are calculated from the equation:

$$R_f = \frac{\text{distance of band from point of application} \times 100}{\text{distance solvent migrates from point of application}}$$

Infrared Spectrophotometry of Resins

With a razor blade or sharp object, the coating is scraped from a 25- by 25-mm (1- by 1-in.) area of the sample sheet. The scrapings are placed in a capped vial. Approximately 0.5 ml of methyl ethyl ketone (MEK) is added to the sample and the extraction of resins is allowed to proceed for approximately 15 to 20 h. The contents of the vial (solvent and clay) are transferred to a centrifuge tube and centrifuged to compact the solids. The liquid layer containing MEK and extracted resins is decanted.

An infrared spectrum is run on a film of the resin extract. The film is prepared by alternately pipetting drops of the decanted material, by using the pasteur capillary disposable pipets, on each of two standard infrared salt plates. With each application the decanted material is dried to evaporate the MEK and to keep the sample area to a minimum diameter (approximately 0.5 cm). The procedure is continued until all the sample has been used. After spotting is completed, the faces of the plates containing the resin samples are pressed together and rotated to break any bubbles containing MEK solvent.

The plates are sandwiched in the sample holder with the faces of the plates containing the resin film to the outside. An infrared spectrum is run on the sample and the spectrum
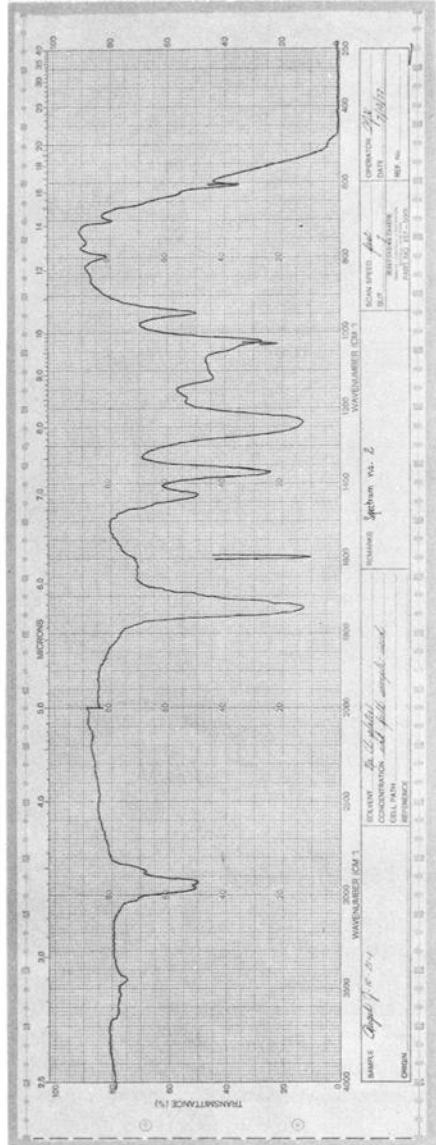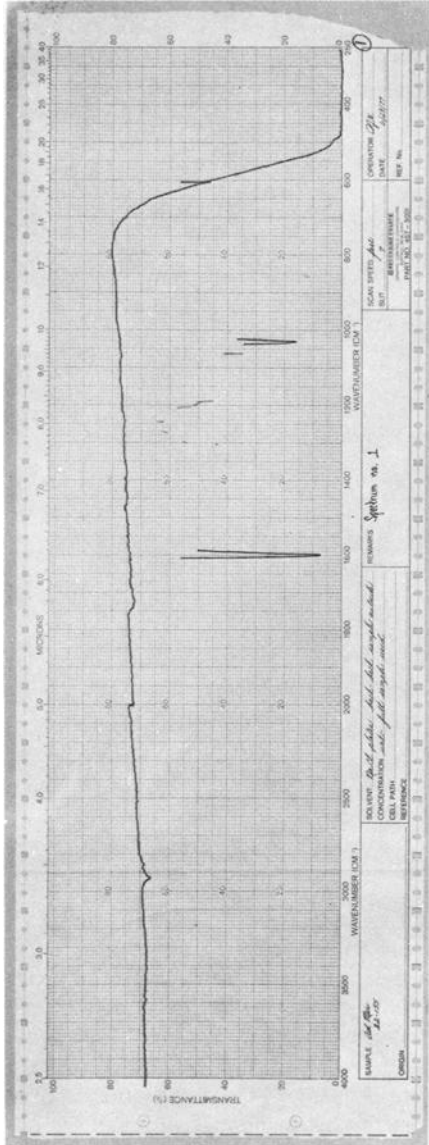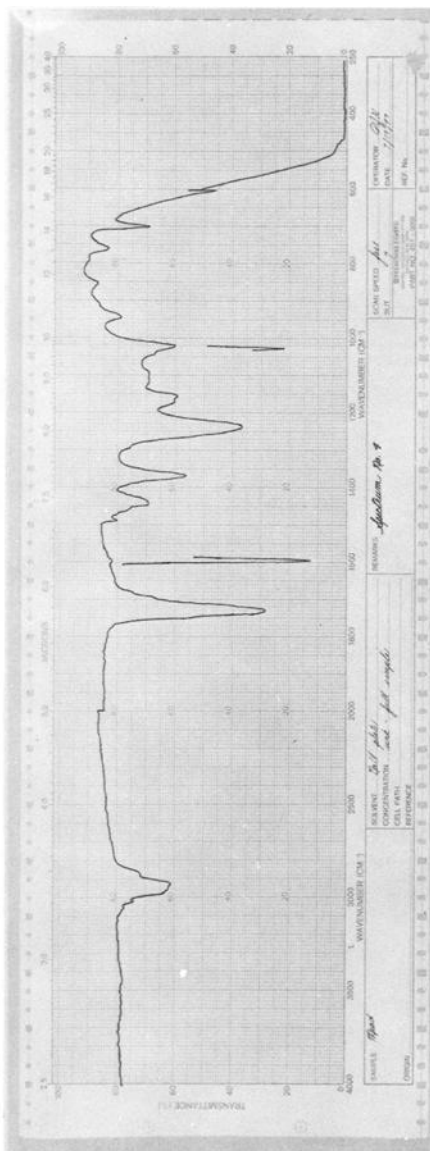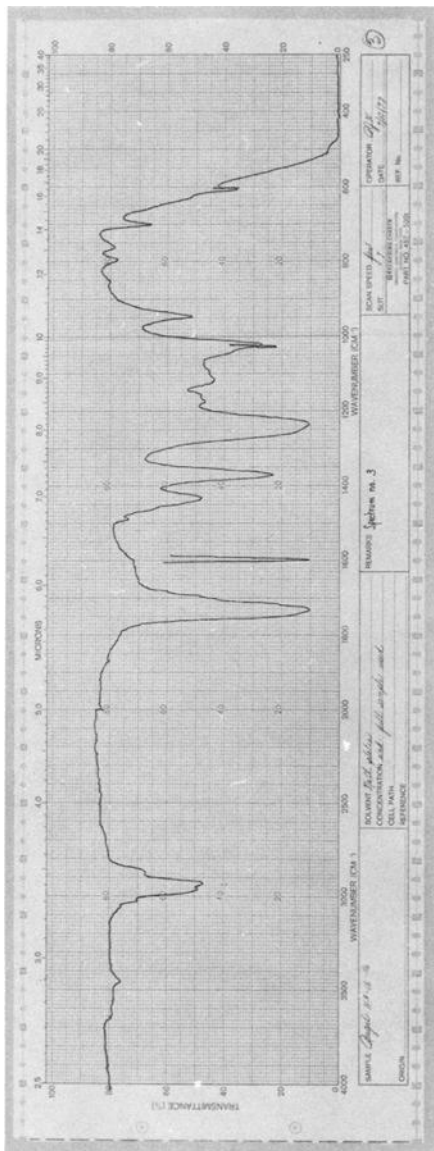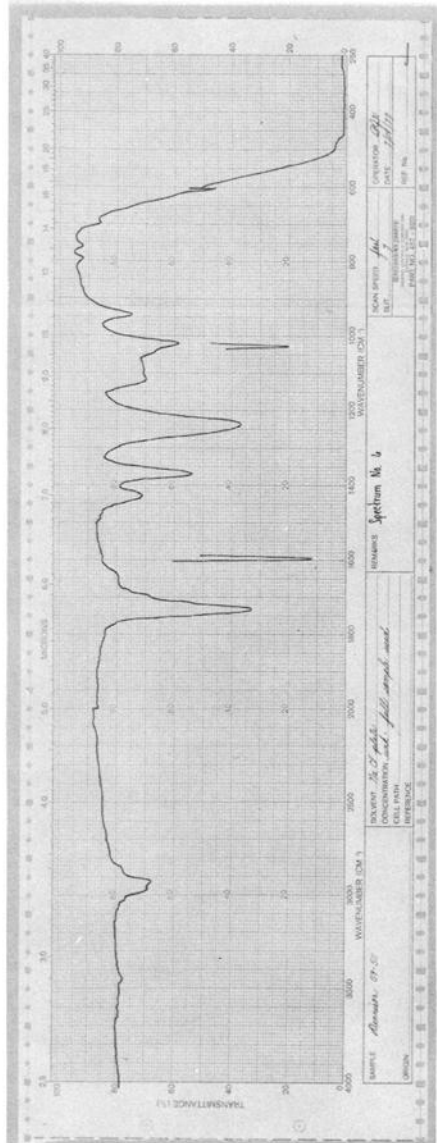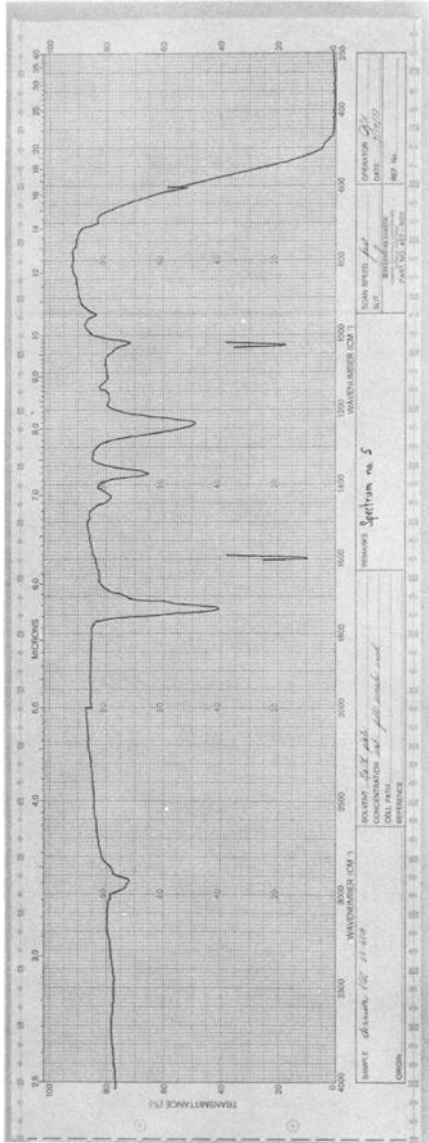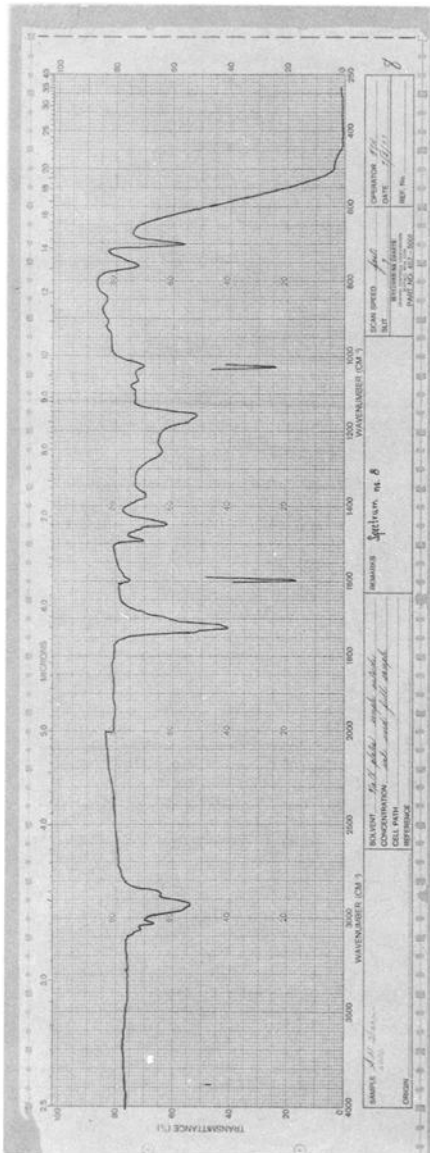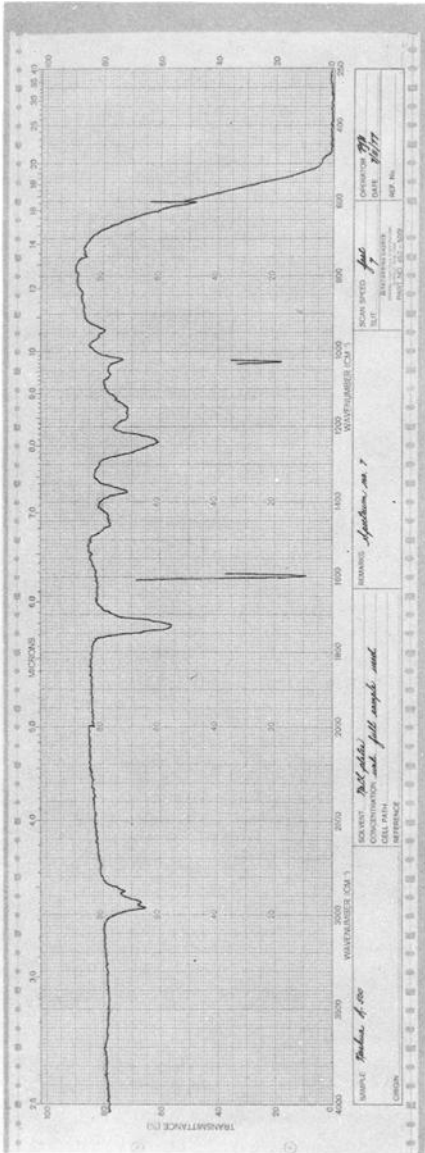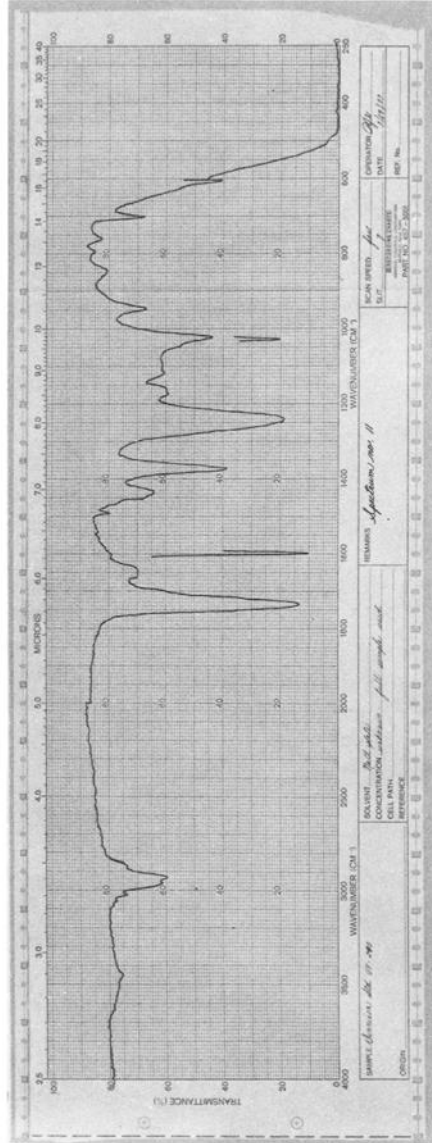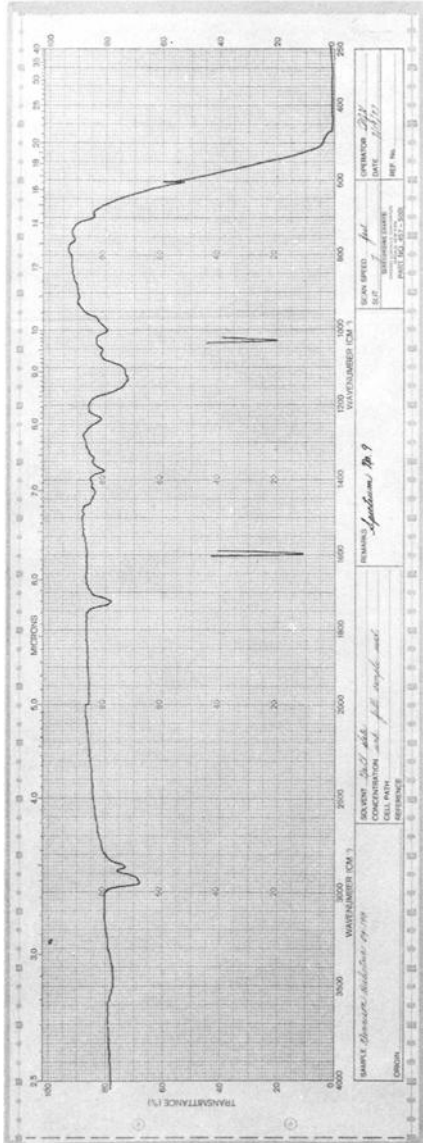
FIG. 1—*The 14 standard spectra.*

FIG. 1—*Continued.*

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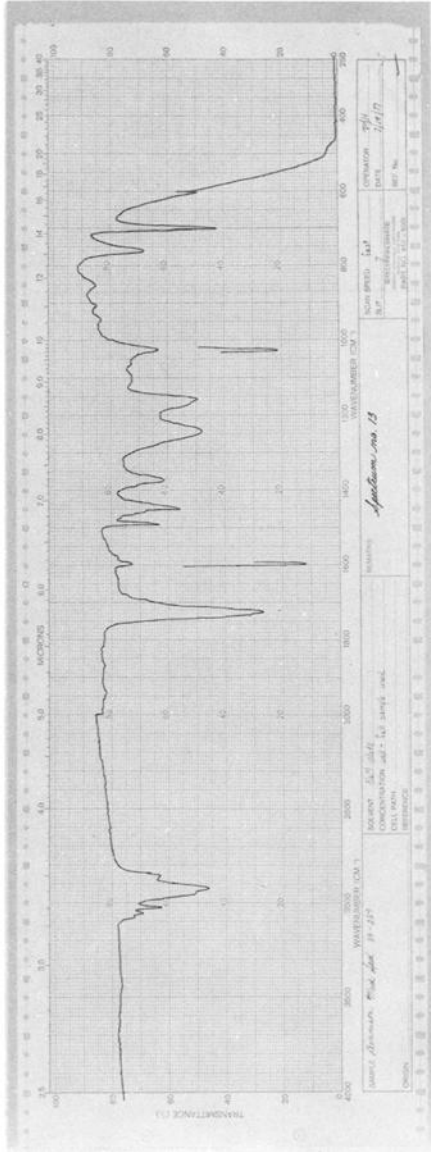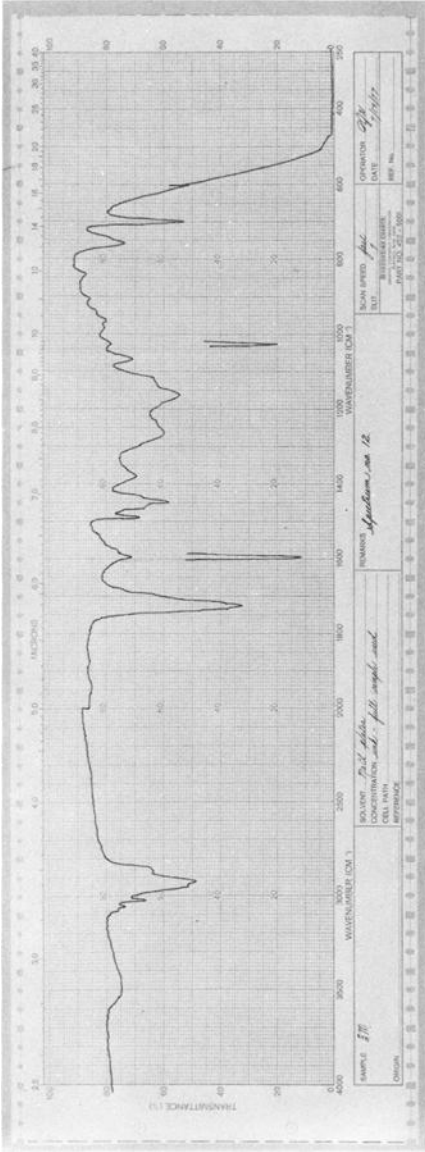
FIG. 1—Continued.

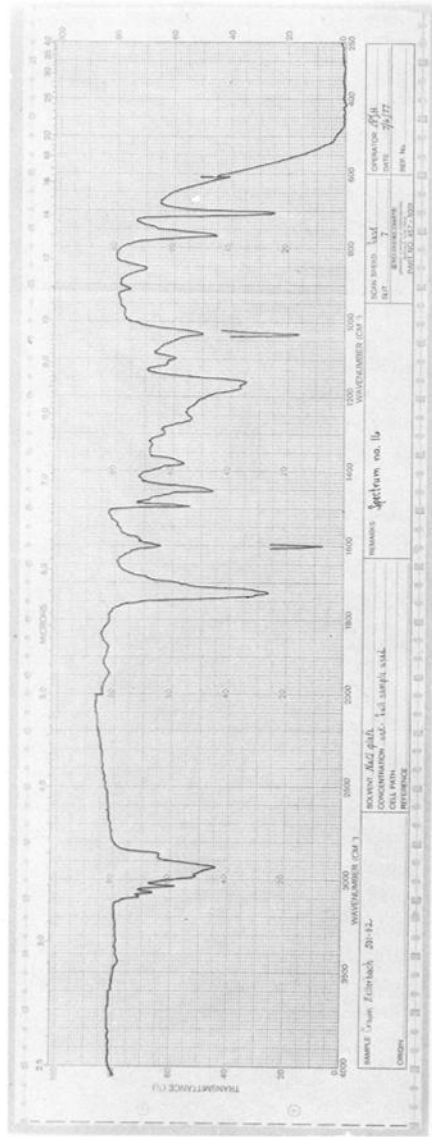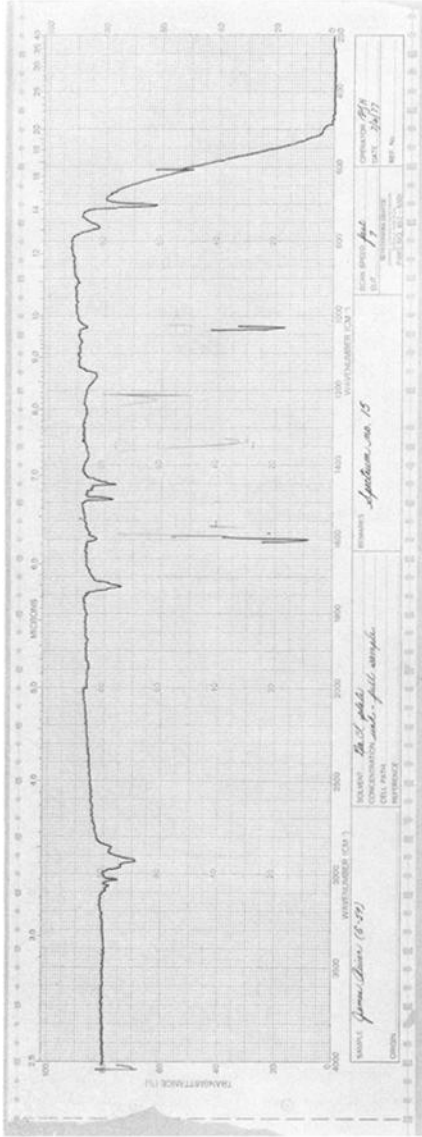FIG. 1—*Continued.*

FIG. 1—Continued.

FIG. 1—*Continued.*

calibrated by using the polystyrene peaks at 1600 and 1029 cm^{-1}. The spectrum is compared to the 14 standard spectra (Fig. 1) and the number of the spectrum corresponding to the sample spectrum is recorded.

Discussion

A semiqualitative flow chart was compiled to facilitate the comparison of the properties of zinc oxide coated papers. The chart is divided into two categories: those samples whose base side, with the application of indicator solution, exhibits the colors red to orange (pH 4.0 to 5.5) and those samples that display the colors yellow to green (pH 6.0 to 7.5).

Weights identified in the flow chart are only approximate in that manufacturers' specifications allow for a 5% weight variation in the base paper and a 2% weight variation in coatings so that the weight of a 50-lb coated paper may range from 46.5 to 53.5 lb.

The R_f values of the TLCs of the sensitizing dyes are listed on the accompanying flow chart (Table 2). Variations in R_f values may be the result of such variables as technique, humidity, and temperature. For that reason, it should be recognized that it is the band pattern which is most significant and the comparison of chromatograms is based on the sequence of bands and their R_f values relative to each other.

The coating extract consisted of acrylate and styrene polymeric resins that for the purposes of this paper have not been specifically identified. No attempt was made to quantitate the infrared peaks; however, when resin extracts exhibited similar peak heights in reverse proportions, the infrared curves were considered to be different spectra. From examination of the spectra it was found that the resin extracts from the 50 different papers could be categorized by 14 different spectra. Each of the spectra was numbered and the appropriate number recorded in the flow chart.

Summary

A procedure was developed to systematically compare and differentiate between zinc oxide coated photocopy papers produced by different manufacturers or by the same manufacturer over an extended time interval. The method uses physical and chemical techniques. The physical (nondestructive) tests consist of weight, pH, and color determinations. Chemical tests require the extraction and analysis of the sensitizing dyes and the resins used in the coated surface. A chart was prepared showing the characteristics of each of the 50 papers used in the procedure.

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