

## SYMPOSIUM ON RESINOGRAPHIC METHODS

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### INTRODUCTION TO RESINOGRAPHY

BY T. G. ROCHOW<sup>1</sup>

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#### SYNOPSIS

Resinography is the graphic description of resins used to explain variations in properties or behavior with changes in composition or treatment. A characteristic graph plots changes in composition with properties and illustrates critical points with macrographs, micrographs, drawings, diffraction patterns, interference phenomena, or absorption spectra.

While resinography is 17 years old, this is the first symposium of its kind on the subject. It presents a brief review of techniques borrowed from metallography, mineralography, petrography, and biology, but the symposium features methods peculiar to the investigation of resins, polymers, and related plastic materials.

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#### HISTORY

Resinography is the graphic study of resins (1). Like its relatives—metallography, mineralography, petrography, ceramography—resinography originated with a description of natural things. For example, in 1924 Nicolardot and Coffignier (2) described and classified rosin and most of the other natural resins which were being used in varnish-making. Their criteria were the etch patterns developed on carefully polished specimens by alcoholic potassium hydroxide or concentrated sulfuric acid. They compared the etching characteristics of different kinds of resins so as to understand better the variations in durability and other practical properties (3).

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While Nicolardot and Coffignier used modified metallographic methods to study natural resins, some other investigators employed biological, chemical, crystallographic, and petrographic methods. For instance, in 1933, Georgi (4) summarized a hundred years' study of rosin acids and their isomers by means of melting point and by optical and crystallographic properties. He showed that many of the old values are not valid and did much to clarify the determinative data. He set the stage for identifying phases which crystallize, for example, from hot rosin size as it is jostled in transit to or agitated in storage at paper mills. As late as 1935 bundles of rosin crystals were mistaken for paper fibers in rosin size. Examination by the present author, employing microscopical procedures long familiar to the biologist, yielded no evidences of the botanical

characteristics of natural paper-making fibers. And optical and chemical tests proved the "fibers" to be crystals of the "3:1 salt" (3 abietic acid: sodium abietate (5)). Then technologists became

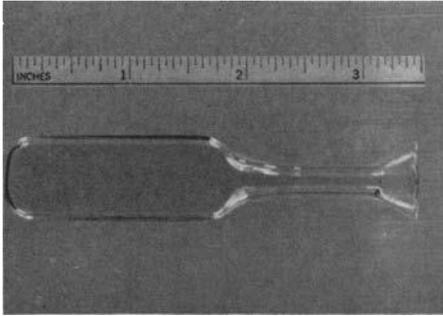


FIG. 1.—The "Kirk" Flask No. 1000 for Incubation of Rosin or Rosin Size and Subsequent Microscopical Examination. (See footnote 2.)

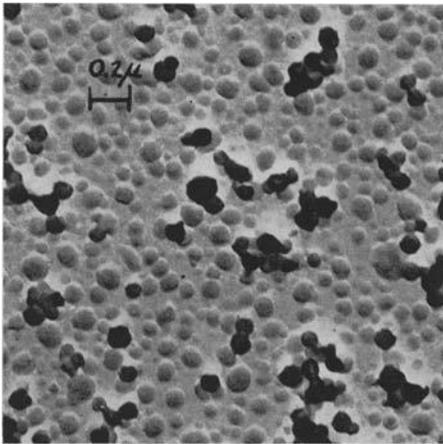


FIG. 2.—Electron Micrograph of an Air-Dried, Typical Rosin-Sizing Solution. (See footnote 5.)

more aware of the crystallizability of rosin itself. Ironically enough, crystallizability was increasing as commercial methods were improving, and the products were becoming purer and purer in rosin acids. Necessity became the mother of invention and prevention. Accelerated tests for crystallizability

were developed by incubating the rosin or its product in a flat vessel<sup>2</sup> which was both easy to fill and easy to examine under a microscope (Fig. 1).

Strazdins improved upon the sensitivity and quantitative aspects of the accelerated test for crystallizability, sometimes seeding the sample with crystals of rosin.<sup>3</sup> Using the test, he found ways of modifying rosin and its products so as to inhibit or prevent crystallization.<sup>3,4</sup> Some other industrial

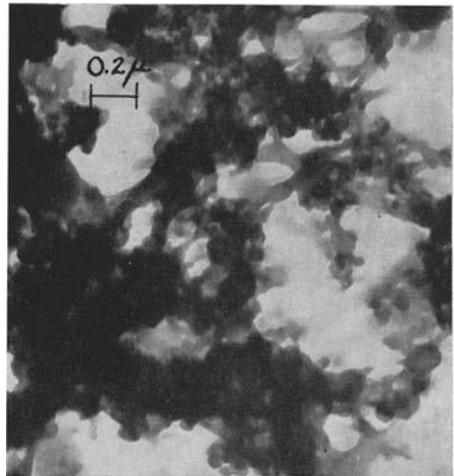


FIG. 3.—Electron Micrograph of Air-Dried Floc of Uranyl Rosinate, Produced Experimentally to Give High Contrast to Particles of Rosin Size. (See footnote 6.)

firms probably now have their own tests of crystallizability in resins, but it might be helpful to both producers and consumers to have a standard ASTM test.

There are many industrial uses for rosin, and understanding the processes leads to control and improvement. For

<sup>2</sup> Devised by the late A. F. Kirkpatrick (Feb. 15, 1956) and furnished as the "Kirk" Flask No. 1000 by R. C. Ewald.

<sup>3</sup> U.S. Patent No. 2,776,275, Jan. 1, 1951. E. Strazdins was assignor to American Cyanamid Co. for this and the following patents.

<sup>4</sup> U.S. Patent No. 2,934,468, April 26, 1960.

example, the mechanism of sizing paper with rosin emulsion and alum has been illustrated in drawings by Lee (6), photomicrographs by Rochow (5), and autoradiographs and electron micrographs by Hock (7). There now remains little doubt that rosin size starts out as a very fine emulsion (Fig. 2)<sup>5</sup> and is flocculated by alum (5).

Botty and Woodberry<sup>6</sup> used 0.4 per cent uranyl acetate [ $\text{UO}_2 (\text{C}_2\text{H}_3\text{O}_2) \cdot 2\text{H}_2\text{O}$ ] in some experiments to give

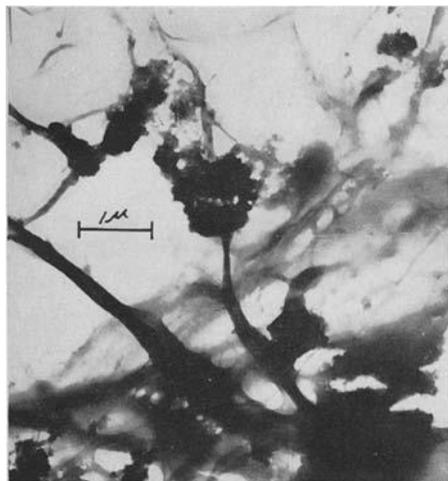


FIG. 4.—Electron Micrograph Showing Flocs of Experimental Uranyl Rosinate Adhering to Fibrils of Air-Dried Pulp. (See footnote 6.)

contrast to the rosin floc in the electron micrographs. Figure 3 is an electron micrograph of an air-dried floc of uranyl rosinate, and Fig. 4 shows that the wet flocs of uranyl rosinate adhere to fibrils which have been air dried. These results are similar to their earlier results and to those of Hock (7), who used the standard technique of shadowing with an evaporated metal. Such a metal is extremely

<sup>5</sup> F. G. Rowe, American Cyanamid Co., Stamford, Conn., unpublished work, August 11, 1953.

<sup>6</sup> M. C. Botty and N. T. Woodberry, American Cyanamid Co., Stamford, Conn., unpublished work, Jan. 4, 1952 to August 11, 1953.

fine-grained, and so, as Botty and Woodberry proved,<sup>6</sup> shadowing does not interfere with the manifestation of the much larger particles of rosin size.

The rosin size *in situ* on the sized paper still remained to be shown. This was to be done by replication, but heat or solvent would change the location of the rosin. Therefore Felton, Botty and Clark (8), devised a technique for exerting localized pressure under a steel ball onto the back of the specimen lying on a cast

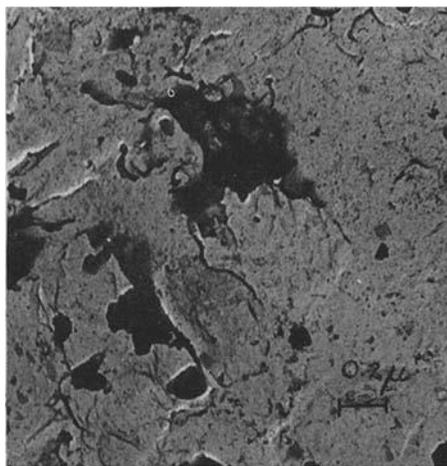


FIG. 5.—Electron Micrograph of Two-Step Replica of the Brittle Fracture of Rosin.

thin film of ethyl cellulose on glass. They metal-shadowed the impression on the film and then carefully transferred it to the electron microscopical screen. They illustrated their one-step technique with a replica of the unsized hand-made paper. Then they validated the method by employing a blot of India ink to show that the extremely small particles are sharply replicated. That the bright dots represent carbon particles is proved by the fortuitous presence of some carbon particles sticking to the replica instead of remaining with the paper. Next they illustrated their method with replicas of rosin-sized hand sheets made of standard

pulp, rosin size, and papermakers' alum. The investigators found that the rosin floc on the surface of the air-dried sample was particulate, as Hock had reported (7). But Felton, Botty, and Clark found that the drum-dried sheet (representing a commercially calendered one) was not coated predominantly with discrete particles as Hock reported. Neither was there a continuous film of rosin. Instead there was, in this case at least, some degree of fusion, coalescence, and spreading of the rosin-size particles.

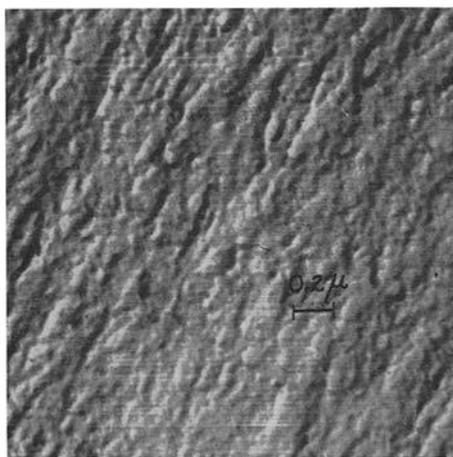


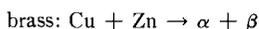
FIG. 6.—Electron Micrograph of Two-Step Replica of the Brittle Fracture of Amber.

As is well known, consolidated rosin is brittle even at room temperature. Figure 5 is an electron micrograph of a two-step replica (gelatin, then silica (9)) of a fracture surface of the type of commercial rosin that is obtained from tall oil. Except for a few bits of rosin embedded in the replica, the fracture of the tall oil rosin is quite without morphology. Presumably gum rosin and wood resin would look much like tall oil rosin.

Amber from Chiapas, Mexico, on the other hand, as illustrated by Fig. 6, shows a particulate fracture surface of the sample that was embrittled in liquid nitrogen. The morphology is much like

that of synthetic melamine-formaldehyde resin (10,11) and other insoluble cross-linked resins. Evidently, amber too is insoluble because it is crosslinked.

Rubber is another natural material which was examined electron microscopically and compared with a synthetic material (12). Natural or synthetic rubbers are alloyed with rosin or its products to produce commercial pressure-sensitive adhesives. Hock and Abbott (13) and later Hock (14), studied such systems electron microscopically. They found that, for optimum adhesion according to the Wetzel (15) test, a two-phase system was required of the components. Hock (14) concluded that morphology, composition, and adhesion are generally correlated. In the range of compositions yielding good adhesion there is not only the continuous phase,  $AB$ , of the resin,  $A$ , dissolved in the rubbery material,  $B$ , but also a discontinuous phase,  $B'A$ , of the rubber low in molecular weight,  $B'$ , dissolved in the resin  $A$ . The reaction, within limits of ratios of  $A:B$ , may be written:  $A + B \rightarrow AB + B'A$ . This is something like the reaction of one metal, such as copper, with another, such as zinc, in such ratios under such conditions as to give a polyphase alloy, say:



In polyphase alloys the separate phases contribute more or less different properties. For example, in  $\alpha + \beta$  brass, the  $\alpha$  phase contributes ductility while the  $\beta$  phase contributes strength. In the pressure-sensitive adhesives, the continuous, rubbery phase,  $AB$ , permits conformation with the texture of the host-surface while the particulate, tacky phase contributes points of adhesion. Hock (14) very closely correlates the electron micrographs with points on the graph, plotting tackiness in grams for the  $\frac{1}{16}$ -in. diameter probe (15) with

concentration as per cent tackifying resin in rubbery substance.

#### MODERN RESINOGRAPHIC METHODS AND THE PROGRAM OF PAPERS

Hock's study is a nice example of modern resinography on the most practical level, that of the material itself. There are many other examples, including all the papers in this symposium. They illustrate a variety of techniques used to describe, analyze, and understand the properties of a variety of materials, all falling into the broad category of "resins (16,17)."

At first, resins were natural, nominally amorphous, plastic materials, varying from rosin, which is monomeric and brittle, to rubber, which is highly polymeric and very extensible. Modifications of natural materials, such as ester-gums, hard rubber, or cellulose ethers, are also classified as resins. But the main impetus to develop and improve resinographic methods has sprung from the great growth and development of synthetic polymers, thermoplastic, "elastic," and thermoset (18). Then too studies of composites of resins with other materials such as glass, ceramics, minerals, and metals are generally resinographic (5). That is, the techniques of preparation and examination generally must be tailored to the requirements of the resin in contact with harder material. There are also technical requirements in problems which involve examination out to the very edge of the specimen (1).

In this symposium Gedney and Thomas discuss modern solutions to the problems of preparing polished surfaces of resins for examination by reflected light. Then Wright and Hall discuss specific techniques for studying transparent sections of resins between crossed polars. They also introduce the need of the resinographer to study mechanisms by high-speed cinematography.

Mogensen gives another example, that of observing the fiber-forming process and the relevant changes in optical properties and strength. Nahmmacher proceeds to analyze birefringence in terms of that part which is inherent in the crystals (natural orientation) and that which is the result of flow (including man-made orientation).

The above are primarily microscopical techniques. Scheier and Lyons present their method of describing the surface of fibers by probing with a razor's edge. Sloan describes filaments by means of light-scattering. Rhodes and Stein study the light scattered by the internal structure of both fibers and films. Scott discusses various techniques for examining the internal structures of fibers.

There are various ways a microscope can be designed or modified to increase the visibility of morphology and structure. Morehead and Felton illustrate the resinographical use of phase microscopy by both transmitted and reflected light. Some applications of modern ultraviolet microscopy in resinography are described by Felton, while Zieler discusses fluorescence of resins in ultraviolet light. McCrone discusses very recent applications of dispersion staining to the identification of resins.

Grabar and Chen describe a modern application of the Berek compensator—which is to study the polymerization of a crystalline monomer. Newman discusses resinography by means of X-rays. Botty illustrates electron microscopical techniques with the description of a polyphase, polymeric system. Claver returns to phase microscopy to describe such systems.

Coulehan concludes the symposium with a cinematographic study of the mechanism of failure in some resins by stress crazing as a result of some types of wetting.

## PURPOSES OF THE SYMPOSIUM

These papers largely reveal the present state of resinography. The subject is very timely. While resinography has been largely neglected in the past very recently there was a national symposium on the correlation of morphology, composition, and properties of polymers (19). So it is appropriate to discuss methods of preparation and study.

A second purpose of this symposium is to indicate future resinographic tasks which may be in the realm of ASTM. Such tasks might pertain to bibliography,

Moreover, the level of molecular organization on which the resin is being described, analyzed (or synthesized), and tested should be understood. Four levels pertain to (1) discrete molecules, (2) molecules arranged in one or two directions, (3) molecules spacially arranged in one phase, and (4) the practical material itself (often polyphase) (10). Organization of molecules on these four levels of increasing complexity is charted in Table 1. It is hoped that such a system will facilitate the correlation of data

TABLE I.—FROM MOLECULE TO MATERIAL.

Level	Description	Composition	Properties
I. ....	molecule	atoms	chemical
II. ....	surface	molecules	interfacial
III. ....	phase	molecules	respective
IV. ....	material	phases	industrial

nomenclature, preparation of samples, methods interpretation of results, and future symposia.

A third purpose is to appraise the extent of interest of the Society in resinography.

All three purposes depend upon an understanding that resinography is concerned with description, composition, and properties, no matter what instrumentation is involved. Some methods not covered in this symposium are nuclear magnetic resonance, molecular weight determination, infrared spectrometry, and X-ray diffraction.

throughout the symposium and in the future.

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Jean Langenheim of the Biological Laboratories of Harvard University furnished the sample of amber, and the author gratefully acknowledges her initiation of the resinographic study of this material.

Acknowledgment is also made of the work of Miss Irene Piscopo and Mr. Martin C. Botty in the electron microscopical studies.

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## DISCUSSION

JACK CAZES.<sup>1</sup>—I am new to the field of resinography. The most difficult decision that I have to make is whether to get one microscope equipped to do a series of different jobs, or several microscopes, each equipped to do a specific job. One factor to consider in the case of a "universal microscope" is the time required to convert from one mode of operation to another; a second factor is the possibility that more than one individual might want to use the equipment for different purposes at the same time.

One big problem for a novice resinographer is deciding just what kind of equipment is required to do a specific job. Should he purchase a phase contrast, polarizing, interference, X-ray, electron, ultraviolet, or other type of

microscope? Will he need specialized photographic equipment or will a simple 35-mm or Polaroid camera do?

Are there any good articles or books available on any of the specific resinographic techniques or on resinography in general? One could use these, at least, as a "departure" point. This symposium has served this purpose to a certain extent, and I would like to see ASTM continue this work in the future.

T. G. ROCHOW (*author*).—First assume that a resinographer will link compositions and treatments with properties by careful *macroscopical examination*, with or without a simple magnifier.

The first *microscopical* step in resinography, in my opinion, is to look with a stereoscopic (binobjective, binocular Greenough-type) microscope.<sup>2,3</sup> Of all

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<sup>2</sup> T. G. Rochow, "Resinography," *Encyclopedia of Microscopy*, G. L. Clark, ed., Reinhold Publishing Corp., New York, 1961, p. 532.

compound microscopes, the stereoscopic type has the greatest working distance and depth of focus so that a great variety of resinous samples generally need no preparation or very little. It is inexpensive enough for most employers to supply one for each investigator. The image is

readily and easily do a large variety of jobs concerned with manipulation of and operating on the specimen—including heating, cooling, stretching, scratching, cutting, or dissecting it. The stands are versatile, and the transfer from reflected to transmitted illumination is simple

TABLE 2.—THEORETICAL RESOLVING POWERS OF LIGHT MICROSCOPES.

Focal Length, mm	Numerical Aperture, $NA$	Maximum Useful Magnification	Approximate Theoretical Limit of Resolution, $d^a$		Depth of Field
			Axial, $\mu$	Oblique, $\mu$	
250.....	0.01	eye alone, 1 time	100	...	...
25.....	0.1	hand lens, 10 times	10	...	42
32.....	0.1	stereoscopic, compound microscope, 100 times	5	2.5	25
16.....	0.25	monobjective, compound microscope, 250 times	2	1	3.8
8.....	0.50	monobjective, compound microscope, 500 times	1	0.5	0.86
4.....	0.95	limit, air-immersion objective, 1000 times	0.52	0.26	0.083
3.....	1.38	oil immersion (5000 Å), 1500 times	0.36	0.18	...
3.....	1.38	oil immersion (quartz ultraviolet 2700 Å), 2000 times	0.20	0.09	0.04

<sup>a</sup> Based on Abbe's theory:  $d = \lambda/(1 \text{ to } 2 NA)$  (disregards aberrations).

This is about *maximum* obtainable resolution and assumes adequate contrast. Any reduction of aperture of objective or condenser reduces  $d$ . Photography has its own limitations.

TABLE 3.—THEORETICAL RESOLVING POWERS OF ELECTRON MICROSCOPES.<sup>a</sup>

Accelerating Volts, kv.	10	20	50	100	200	500	1000
Wavelength $\lambda$ electrons, Å	0.122	0.086	0.054	0.037	0.025	0.014	0.009
Resolution $d$ , Å	3.7	2.9	2.1	1.7	1.3	0.9	0.7

These *theoretical* values are for an electromagnetic lens of special design not yet available. The values further assume no astigmatism, centering of illumination and lenses, no fluctuating magnetic fields, stability of lens currents and accelerating voltage, and sufficient illumination without overheating the specimen. Presently, with the best conventional electron microscopes operated under optimum conditions, the practical limiting resolution is about 10 to 20 Å.

<sup>a</sup> E. Ruska, "Electron Microscopy," Fifth International Congress, Philadelphia, 1962, S. S. Breese, Jr., ed., Academic Press, New York, 1962, Vol. 1, A-1.

natural-looking, three-dimensional and upright; a novice can see and interpret the image without practice, effort, or squinting. He can convert from transmitted to reflected illumination easily and quickly. For these reasons he can

Time to convert from one mode of operation to another is negligible. Focusing is not delicate so that one can confidently show the object to another person with little or no adjustment. In fact, projection may be done with one ocular while the specimen is scanned through the other. Likewise one may observe with one ocular while he photomicrographs through the other. With

<sup>3</sup> T. G. Rochow, "Chemical Microscopy," *Encyclopedia of Chemistry*, G. L. Clark, ed., Reinhold Publishing Corp., New York, 1957, Fig. 1, p. 221.

simple adapters he can use either a standard 35-mm or Polaroid camera to suit his purposes and circumstances. Simultaneously rotatable polars (see footnote 3) are strongly recommended so that, with little trouble and expense, crystalline or strain birefringence may be observed, even while changes are occurring. Because of limited resolving power (see the accompanying Table 2), one is limited to observing phenomena on levels III and IV (Table 1 of the paper). They generally involve cracks, fracture-surfaces, surface-defects, inclusions, crystallization, melting, strain-analysis, fibers, layers, striations, etc. Thus many jobs may be done with the one simple, inexpensive instrument. But even if part of the problem remains unsolved, the stereoscopic microscope generally serves to orient or prepare the sample and to indicate the nature of a second microscope that is preferable.

The second microscope may be petrographic (or chemical) if the phenomenon is internally optical, or metallographic if the phenomenon is on the surface (even though transparent). If a petrographic or metallographic microscope needs to be purchased, ease of conversion to phase-contrast, interference, ultraviolet, or infrared should be anticipated as far as experience indicates at the time.

The questions and problems involved in your first two paragraphs are many and complex. I would not attempt to

resolve them fully, even if I could. Degrees of microscopical satisfaction vary with each individual and will change with his experiences. My general advice is to provide enough stereoscopic microscopes, equipped for reflected, transmitted, and polarized light, so that such a microscope is always available for use. For requirements of more resolution than  $5 \mu$ , consult Table 2 on the basis of resolution and working distance. Then consider contrast and quality of image with usual and special methods of illumination. If and when X-ray, electron (Table 3), or emission microscopes are indicated, use the simplest one until the need for a more complicated one is indicated.

The best monograph on resinography and resinographic techniques will be the ASTM Special Technical Publication of this symposium. We planned it so and the Society is proceeding with its publication. Further reading on specific subjects will be indicated by the references. As a departure point, reference (1) of the paper and footnotes 7 and 8 herein are recommended until superseded.

We welcome the suggestion that ASTM continue in resinography. The Board of Directors has recently approved the formation of ASTM Committee E-23 on Resinography. An invitation is being extended to those interested to pursue mutual interests by working on the committee.