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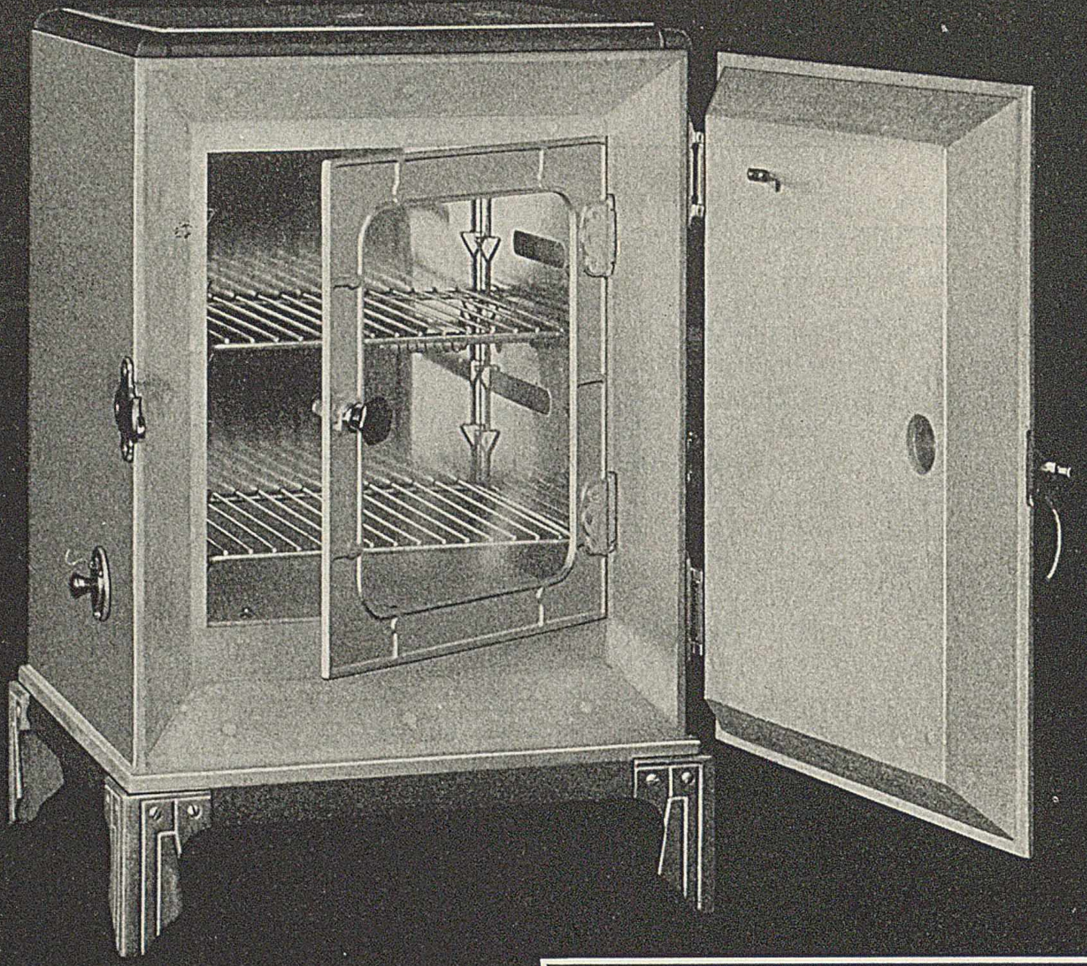

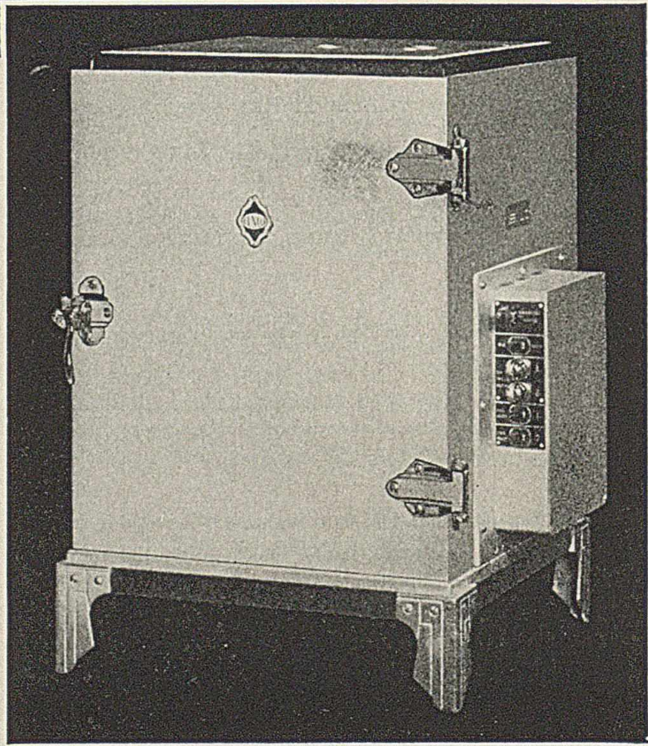

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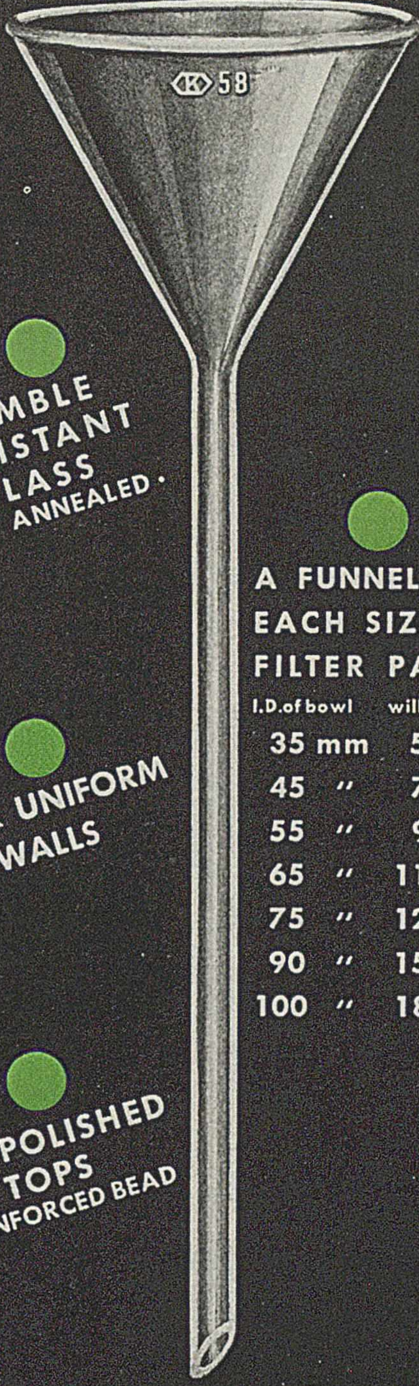

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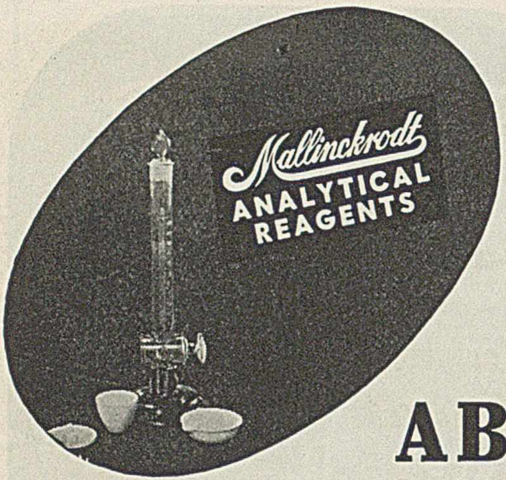

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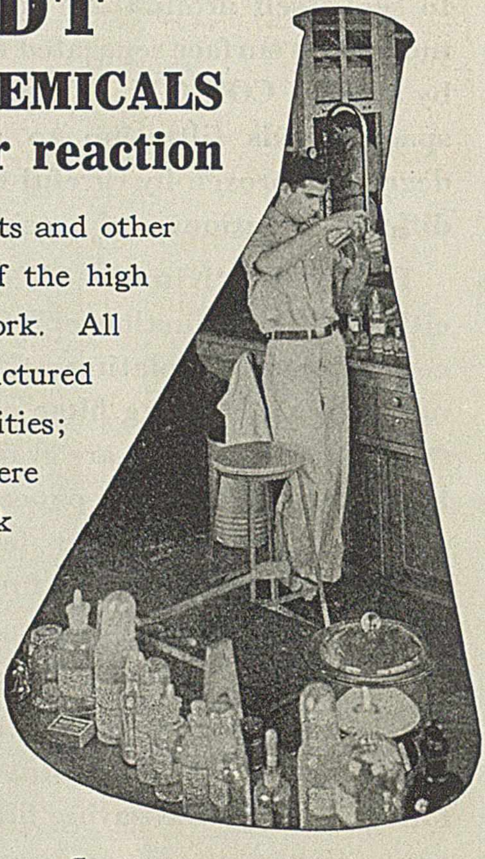

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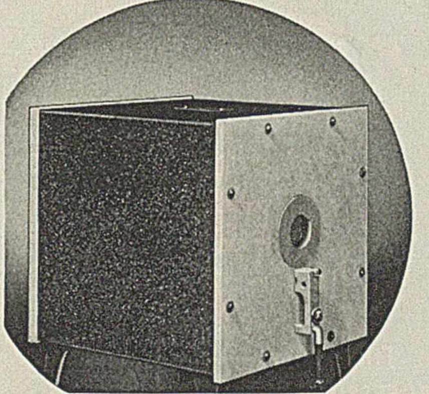

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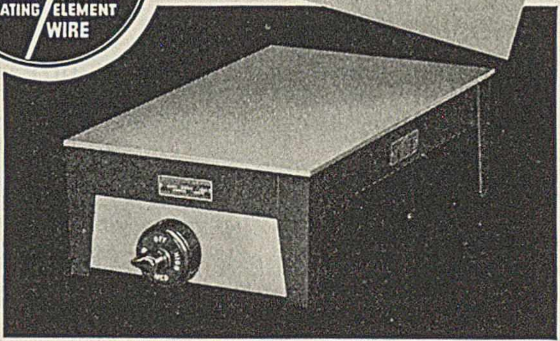

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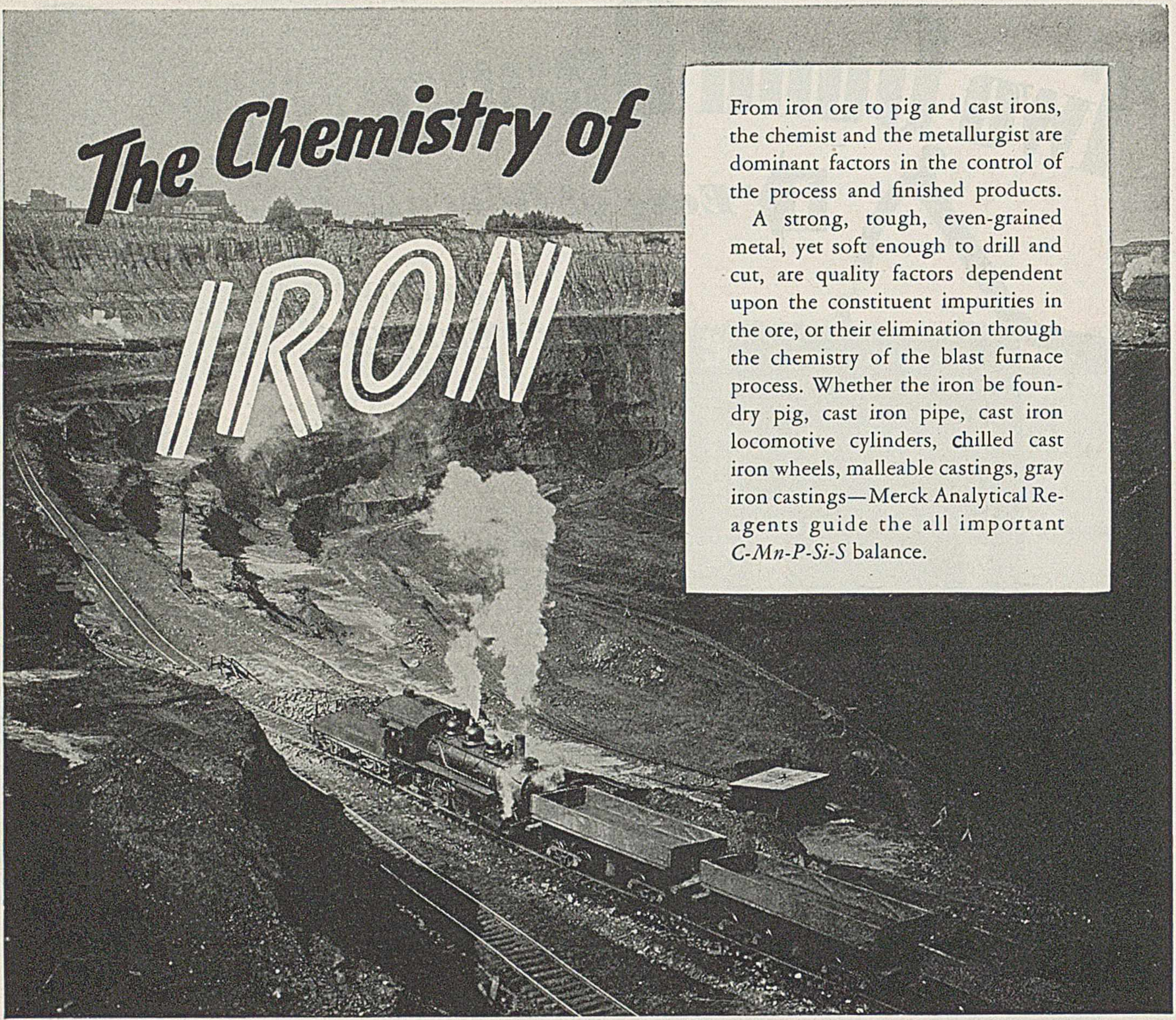

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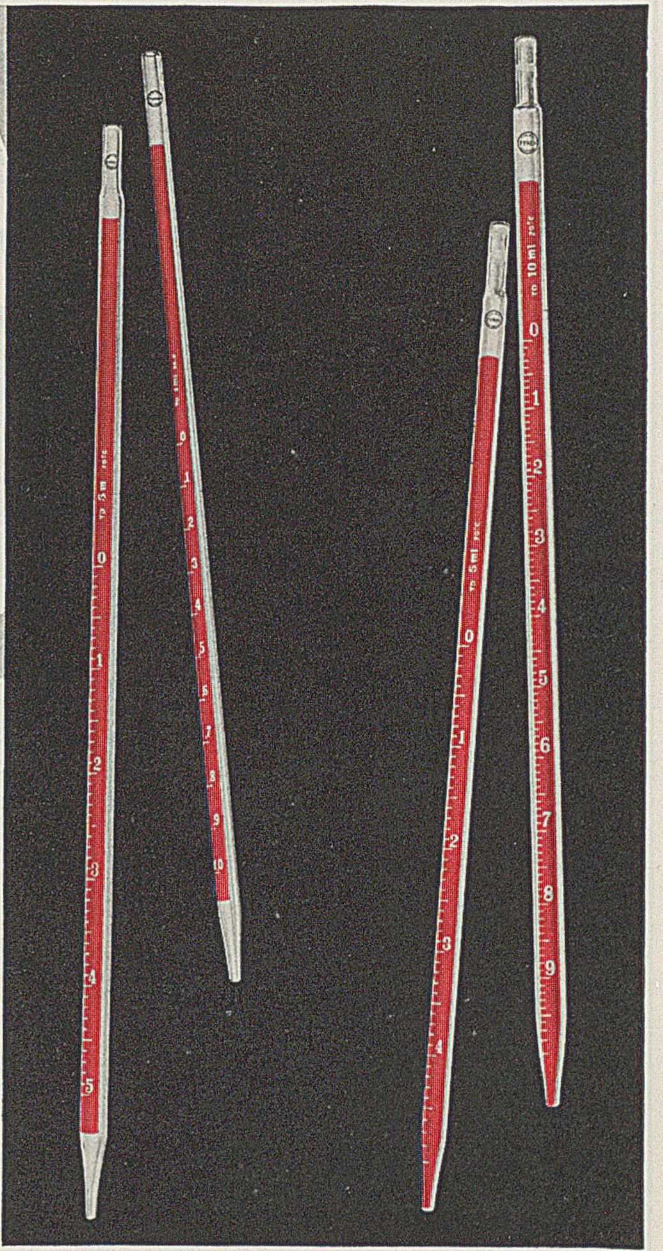

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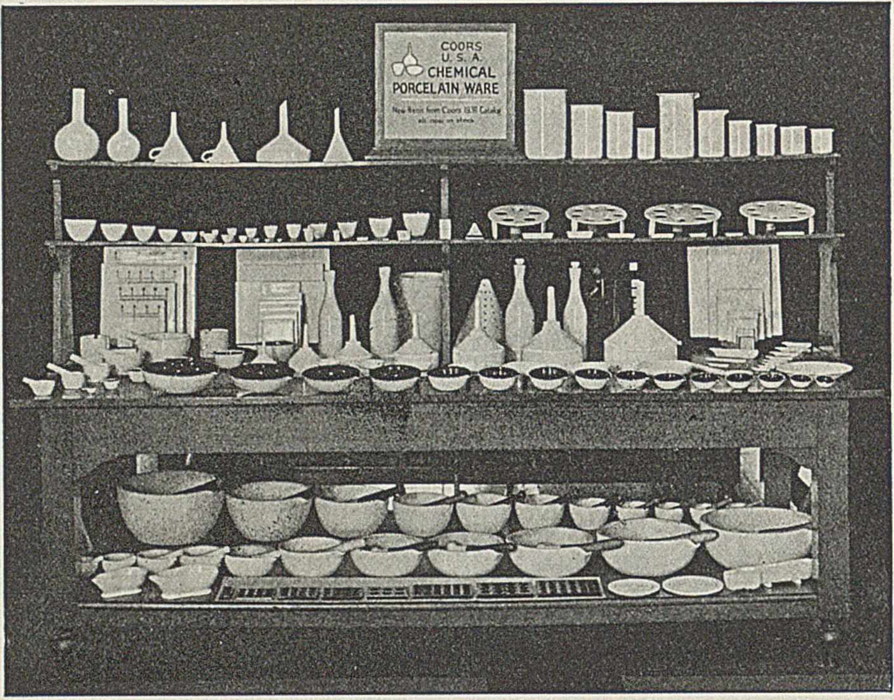

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INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION ◆ Harrison E. Howe, Editor

Identification of Aluminum Hydrate Films

Of Importance in Silicosis Prevention

L. H. GERMER AND K. H. STORKS, Bell Telephone Laboratories, New York, N. Y.

SILICOSIS develops rather quickly in rabbits exposed to air containing moderate concentrations of quartz particles finer than about 5×10^{-4} cm., but is completely prevented if aluminum powder is also present in the air to the extent of about 1 per cent by weight of the quartz powder. This protective action of aluminum powder was discovered at the McIntyre Porcupine Mines, and has been studied experimentally by Denny, Robson, and Irwin (*1*).

It has been established (*1*) that aluminum forms, in the lungs, a protective film upon the surface of silica particles which prevents them from dissolving, and thus prevents toxic effects. The seriousness of silicosis in the mining and foundry industries indicates the importance of identification of this film.

The smallness of the silica particles and the very small amount of aluminum (less than 1 per cent) which is sufficient to cover them with a protective film make it evident that this film is extremely thin. An estimate of its thickness can be readily made from available data.

For a spherical particle of diameter D covered by a film of thickness t, assumed much smaller than D, $t/D = fM\Delta/6$, where f (<0.01) is the ratio of the mass of aluminum in the film of unknown composition to the mass of the silica particle, M is the ratio of the molecular weight of the film to the molecular weight of the aluminum in one molecule of the film, and Δ is the ratio of the density of silica to the density of the film. In this expression Δ is of the order of unity and M of the order of 3. Silicosis is produced by particles for which D lies in the range between 1 and 5×10^{-4} cm., and solubility is prevented by an amount of aluminum which would make $f = 0.01$ if the aluminum were completely utilized in forming films on silica particles. Setting $\Delta = 1$, $M = 3$, $D = 5 \times 10^{-4}$ cm., and $f = 0.01$, one obtains $t = 25 \times 10^{-7}$ cm. = 250 Å. Because many particles are smaller than 5×10^{-4} cm., and available aluminum is surely not entirely used in forming film as is assumed by setting $f = 0.01$, it is certain that protection is afforded by films on silica particles many times thinner than this calculated upper limit of 250 Å.

This estimate gives 250 Å. as the thickness of a film which will certainly prevent solution of silica and toxic effects. The minimum thickness of film which will prevent solution is probably very many times less than this figure.

Considerations such as these, indicating that the protective film on silica particles can be extremely thin, led Francis C. Frary of the Aluminum Company of America to the view that electron diffraction analysis might be the best means of identifying the film. Such an investigation has been carried out by the authors in collaboration with Dr. Frary, and this paper presents an account of their part of the work.

They have found that the material which is precipitated upon silica by the reaction of water and aluminum is a hydrated oxide of aluminum. After drying, the film is crystalline and gives electron diffraction patterns characteristic of the variety of aluminum oxide monohydrate ($Al_2O_3.H_2O$) commonly called alpha-monohydrate in America, sometimes called boehmite, and identical with the natural monohydrate occurring in French bauxite. This conclusion from the authors' experiments has been stated in the second paper by Denny, Robson, and Irwin (*1*). The present paper contains a more detailed account of the electron diffraction experiments upon which the conclusion is based.

Preparation of Silica Films

In electron diffraction studies one frequently obtains much clearer patterns when the primary beam of electrons goes directly through the specimen under examination than when the beam is scattered from its surface. On account of this superiority of the transmission method most of the electron diffraction experiments recorded here were made upon very thin films with the electron beam passing directly through them.

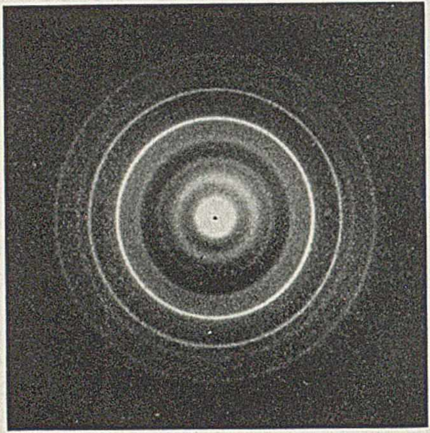
Films of silica, about 200 Å. thick, have been treated under various conditions with water containing aluminum powder. At the end of this treatment a film is caught, from the water surface upon which it is floating, across the jaws of a slit (for a photograph of this slit see *5*, Figure 4) 0.05 mm. in width. This slit is mounted in the diffraction camera and, after the air has been exhausted, a beam of electrons is passed through the film and the resulting diffraction pattern recorded on a photographic plate. Features of this pattern are examined in order to identify the material formed upon the surface of the film.

The films of silica used in these experiments are prepared in the following manner. A glass microscope slide is first covered by gold vaporized in high vacuum from a V-shaped tungsten ribbon. Then immediately in the same apparatus silica is vaporized upon the gold from a second tungsten ribbon (*3*). Distances and quantities of gold and silica are adjusted so that the resulting composite film consists of a layer of silica 2×10^{-6} cm. thick lying upon a layer of gold 30×10^{-6} cm. thick. This composite film is large enough to supply a great many samples of silica which can be used in a large number of experiments. Each sample of silica is prepared, as and when required, by stripping from the glass slide a piece of the composite film 3 or 4 mm. on a side, dissolving the gold in a nitric-hydrochloric acid mixture, and then washing the remaining tiny silica film in several changes of distilled water.

Diffraction patterns from silica films prepared in this manner, not exposed to aluminum and water, are made up of diffuse rings characteristic of an amorphous material. There are no sharp rings which could be attributed to unremoved gold. Measured diameters of the diffuse rings correspond by the Bragg formula to spacings of 3.6 Å., 1.95 Å., 1.2 Å., and 0.81 Å.

Silica, Aluminum, and Water

Reaction at Room Temperature. Many tests have been made upon silica films which have floated for various lengths of time upon surfaces of water maintained at room temperature in beakers which also contain small amounts of aluminum powder. This powder is a special grade of aluminum, supplied by Dr. Frary, which contains very little grease. Because of its comparative freedom from grease it sinks in water, whereas ordinary aluminum powder floats as a mirror-like film on a water surface. The powder that floats on water cannot be used very conveniently with the authors' technique.


A

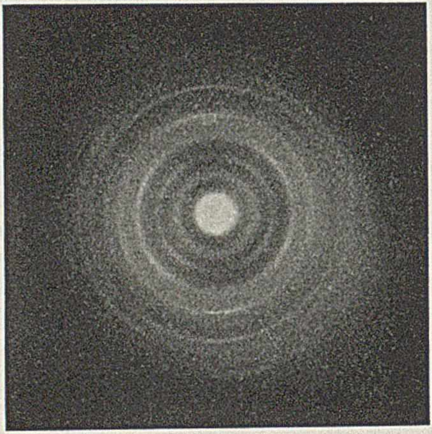

B

Figure 1. Electron Diffraction Patterns from Silica Film Treated for 64 Hours with Aluminum and Water at 38° C.

A. Electron beam normal to film surface
B. Electron beam inclined 45° to film surface, by rotation of film about vertical axis

All silica films that have been treated with aluminum and water at room temperature have yielded diffraction patterns indistinguishable from the pattern from an untreated silica film. One concludes that there is no considerable, or at least no very rapid, production of a surface layer upon silica as a result of the reaction of aluminum and water at room temperature.

Reaction at 38° C. Tests were next carried out at 38° C., approximately body temperature. Films of silica were floated for various lengths of time upon water containing aluminum powder. Many of these films were greatly weakened or even broken up by this treatment, and in order to support them across the narrow slit it was in many cases necessary first to spread an auxiliary supporting foil across the jaws. For this purpose a foil of the plastic material known as Formvar about 200 Å. thick was placed across the slit, and the silica film to be studied removed from the water upon this foil.

Diffraction patterns from all silica films treated with aluminum and water at 38° C. exhibit rings which are more or less sharp. Diameters of these sharp rings are the same on patterns from all the silica films which have been treated with neutral or alkaline water containing aluminum.

Characteristics of these sets of rings, other than their diameters, vary with experimental conditions. The widths of the rings and their absolute intensities, as well as the widths and intensities of particular rings of a pattern relative to other rings of the same pattern, are functions of the duration of the chemical treatment, the pH of the aluminum-water mixture, and the material of the beaker in which it was contained. A description of these peculiarities and their interpretations will be given below, after the identification of the material giving rise to the patterns has been described.

In Figure 1, *A* and *B*, are reproduced diffraction patterns from a silica film which had floated for 64 hours upon water at 38° C. containing aluminum powder in a paraffin-lined glass beaker. The pattern of *A* was obtained with the film normal to the primary electron beam and that of *B* with the film inclined by 45°, rotated from the normal position about a vertical axis as the pattern appears here. The pattern of Figure 2 was obtained at normal incidence from a silica film which had floated for 44 hours upon the surface of a physiological salt solution, known as Locke's solution, containing aluminum powder and maintained at 38° C. in a paraffin-lined glass beaker. The appearance of Figures 1-*A* and 2 suggests that rings of the two patterns have the same diameters, and careful measurements confirm this indication.

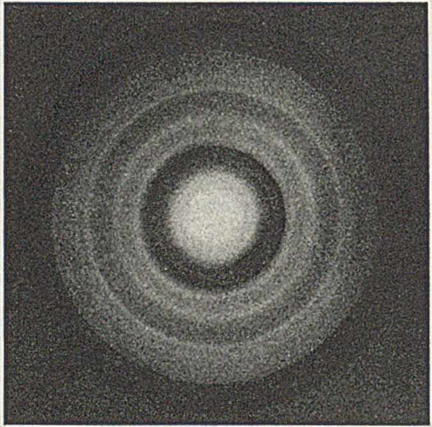


Figure 2. Diffraction Pattern

From silica film treated for 44 hours with Locke's solution containing aluminum

In the first two columns of Table I are measured diameters and estimated intensities of the diffraction rings of Figure 1-*A*. In the third column are values of d, the corresponding crystal spacings calculated from the measured diameters, D, by means of the Bragg formula which, for these experiments, can be written in the form $dD = 2L\lambda$. Here $L\lambda$, the product of the specimen-plate distance and the electron wave length,

TABLE I. COMPARISON OF THE RINGS OF FIGURE 1-*A*, WITH X-RAY AND ELECTRON PATTERNS OF ALUMINUM ALPHA-MONOHYDRATE

Electron Pattern of Figure 1-*A*			Aluminum Alpha-Monohydrate: X-Ray Pattern (from Table II)		Aluminum Alpha-Monohydrate: Electron Pattern (Table III, Figure 6)		
Measured diameters *Mm.*	Estimated intensities (arbitrary scale)	Crystal spacings Å.	Crystal spacings Å.	Estimated intensities (arbitrary scale)	Crystal spacings Å.	Estimated intensities (arbitrary scale)	Crystal Planes
			6.2	10	6.3	4	.
10.3	9	Fuzzy band	..	.	..	.	.
12.8	1	3.66	..	.	..	.	.
14.7	7	3.18	3.17	8	3.21	7	.
20.1	6	2.33	2.35	8	2.34	6	.
..	.	..	2.06	3	2.04	1	.
..	.	..	1.98	2	..	.	.
25.3	10	1.85	1.86	8	1.88	7	3
26.3	1	1.78	1.77	2	1.79	2	.
28.5	1	1.64	1.66	3	1.67	3	.
..	.	..	1.53	2	1.55	1	.
32.6	9	1.44	1.45	4	1.45	5	5
..	.	..	1.44	3	..	.	.
..	.	..	1.39	2	1.40	1	.
35.7	5	1.31	1.31	4	1.32	5	.
..	.	..	1.260	1	..	.	.
38.5	2	1.219	1.210	1	..	.	.
..	.	..	1.180	1	1.172	2	.
..	.	..	1.161	1	1.155	3	.
41.3	8	1.135	1.136	2	1.042	2	8
..	.	..	1.119	1	..	.	.
..	.	..	1.050	1	..	.	.
45.8	1	1.023	1.028	1	..	.	.
..	.	..	0.954	1	..	.	.
..	.	..	0.935	1	..	.	.
51.0	3	0.920	0.925	2	0.909	3	12
54.6	1	0.858	..	.	0.856	2	.
56.7	2	0.827	..	.	0.832	3	.
..	.	..	..	.	0.803	1	.
60.7	2	0.772	..	.	0.774	1	.
65.6	1	0.715	..	.	..	.	20
71.0	1	0.660	..	.	0.666	1	.
..	.	..	..	.	0.614	1	.

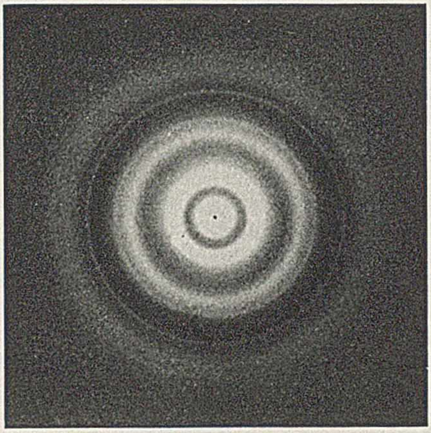


FIGURE 3. DIFFRACTION PATTERN AT NORMAL INCIDENCE

From very thin layer of aluminum hydrate deposited upon supporting foil of Formvar

is known by independent calibration to have the value 2.345×10^{-6} sq. mm.

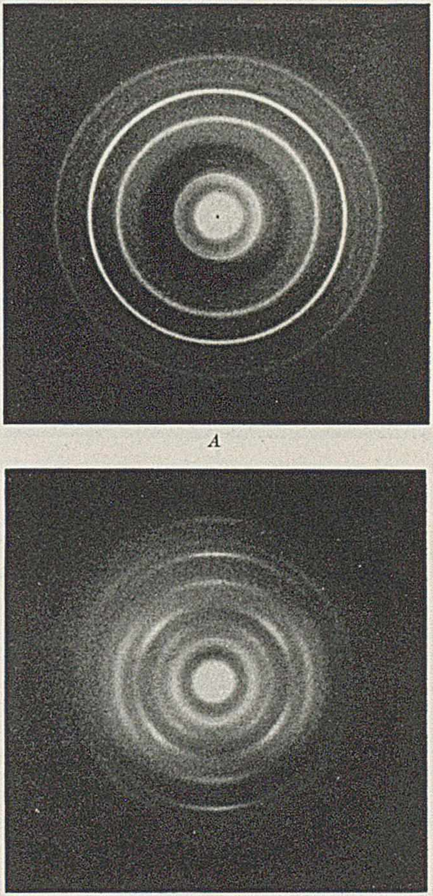
Identification of Protective Layer on Silica

The authors were induced by the work just described to carry out experiments upon hydrated oxides of aluminum. A solution of aluminum chloride in water was precipitated by ammonium hydroxide, and the resulting suspension washed by dialysis for 10 days; after this treatment a very small amount of hydrochloric acid was added. The suspension was found to be stable for a long period of time, and some of it was used in many different experiments.

In the first of these experiments a drop of the suspension was placed upon a Formvar foil lying across the 0.05-mm. slit, and the water was allowed to evaporate. The electron diffraction pattern obtained from this foil at normal incidence is reproduced as Figure 3. The diffuse rings of this pattern were produced by the supporting Formvar foil and the sharp rings by crystals of the hydrated aluminum oxide. A pattern from this same foil at 45° incidence contains, in addition to the diffuse rings, only short arcs crossing that diameter of the pattern which is parallel to the axis about which the foil was rotated; these arcs are portions of imaginary circles which have precisely the same diameters as the rings of Figure 3. Diameters of these rings are related to each other as the square roots of the whole numbers 3, 5, and 8, and they are furthermore the same as the diameters of the three strongest rings of Figure 1-*A*, which are designated by the numbers 3, 5, and 8 in the last column of Table I.

A considerably thicker layer of hydrated oxide was precipitated upon another Formvar foil with the aid of a potential of 3 volts between the slit, upon which the foil was mounted, and an electrode in the suspension. Diffraction patterns from this foil, at normal and at 45° incidence, appear in Figure 4. These are strikingly similar to the patterns of Figure 1, and measurements of the rings of Figure 4-*A*, disclose that there is excellent agreement between the two patterns with the exception of two rings of Figure 4-*A*, which are not present in the pattern of Figure 1-*A*. These are described below.

In still another experiment a foil of Formvar was treated in exactly the same way as the silica film from which the diffraction patterns of Figure 1 were



A

B

FIGURE 4. DIFFRACTION PATTERNS FROM RELATIVELY THICK LAYER OF ALUMINUM HYDRATE UPON FORMVAR SUPPORTING FOIL

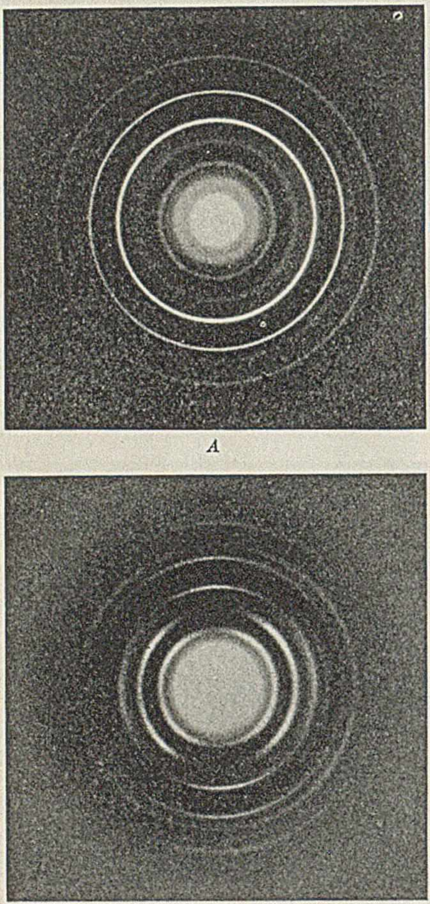
A. Normal incidence
B. 45° incidence

Table II. Data from X-Ray Diffraction Patterns of Hydrated Alumina

Alpha-Monohydrate (Boehmite)				Alpha-Trihydrate (Hydrargillite)				Beta-Trihydrate (Bayerite)			
Measured diameters	Estimated intensities	d, Calcd. as: CuKα	CuKβ	Measured diameters	Estimated intensities	d, Calcd. as: CuKα	CuKβ	Measured diameters	Estimated intensities	d, Calcd. as: CuKα	CuKβ
Mm.		Å.	Å.	*Mm.*		Å.	Å.	*Mm.*		Å.	Å.
28.5	10	6.20	..	32.9	4	..	4.82	33.3	5	..	4.77
50.7	4	..	3.14	36.5	9	4.85	..	37.0	10	4.79	..
56.2	8	3.17	..	40.8	6	4.35	..	40.6	8	4.37	..
68.6	3	..	2.34	53.9	2	3.30	..	49.7	2	..	3.21
76.5	8	2.35	..	57.0	2	3.13	..	55.3	6	3.22	..
87.7	3	2.06	1.85	67.0	2	2.67	..	65.8	1	2.72	..
91.4	2	1.98	..	73.8	5	2.43	..	72.4	6	..	2.22
98.0	8	1.86	..	75.8	5	2.37	..	75.3	4	2.38	..
103.1	2	1.77	..	79.7	3	2.26	..	80.7	10	2.23	..
110.2	3	1.66	..	83.3	3	2.17	..	90.3	3	2.01	..
114.9	1	..	1.43	89.2	4	2.03	..	94.7	4	..	1.72
120.6	2	1.53	..	91.5	4	1.97	..	105.8	7	1.73	..
128.1	4	1.45	..	94.8	3	1.91	..	111.0	1	1.65	..
129.7	3	1.44	..	102.0	4	1.79	..	114.3	3	1.61	..
134.8	2	1.39	..	104.8	4	1.74	..	117.8	3	1.57	..
144.0	4	1.31	..	109.4	4	1.68	..	127.3	4	1.46	..
150.9	1	1.260	..	117.5	1	1.57	..	134.2	3	1.38	..
158.0	1	1.210	..	128.2	3	1.45	..	140.6	4	1.34	..
163.1	1	1.180	..	133.4	3	1.40	..	157.2	3	1.22	..
166.2	1	1.161	..	138.7	2	1.35	..	162.4	2	1.18	..
170.9	2	1.136	..	142.7	2	1.32	..	170.0	1	1.14	..
174.2	1	1.119	..	152.8	2	1.245	..	175.3	2	1.11	..
189.0	1	1.050	..	158.0	2	1.210	..	184.2	1	1.07	..
194.0	1	1.028	..	161.4	1	1.190	..	..	..	..	..
215.3	1	0.954	..	174.1	1	1.118	..	..	..	..	..
222.0	1	0.935	..	182.2	1	1.079	..	..	..	..	..
225.1	2	0.925	..	..	.	..	..	..	..	..	..

obtained—floated for 64 hours upon water at 38° C. containing aluminum powder in a paraffin-lined glass beaker. From this Formvar foil the patterns of Figure 5 were obtained.

Although there are clearly observable differences between the diffraction patterns of Figures 1 to 5, it is certain that they were produced by the same crystalline material. The differences between these patterns and their interpretations are discussed below.


A

B

Figure 5. Diffraction Patterns from Formvar Film Treated for 64 Hours with Aluminum and Water at 38° C.

A. Normal incidence
B. 45° incidence

Dr. Frary supplied x-ray diffraction photographs from three different hydrated oxides of aluminum—alpha-monohydrate (boehmite), beta-trihydrate (bayerite), and alpha-trihydrate (hydrargillite)—and with samples of the hydrated oxides themselves. The x-ray photographs were taken with unfiltered copper K radiation upon cylindrical films with specimen-film distances of 57.3 mm. The measured diameters and estimated intensities of diffraction rings upon these patterns are given in Table II, together with values of spacing *d*, calculated from the measured diameters by means of the Bragg formula. It is clear that some of the diffraction lines are due to copper Kβ radiation, and these have been so designated; in some cases there is an uncertainty.

The calculated spacings and estimated intensities for aluminum alpha-monohydrate from Table II are written down again in the fourth and fifth columns of Table I. Comparison of these values with those from the electron diffraction pattern of Figure 1-*A*, indicates excellent agreement, except for the absence from the electron pattern of the reflection corresponding to 6.2 Å. which is extremely strong in the x-ray pattern, and for the presence in the electron pattern of a diffuse band of diameter 10.3 mm. and of a very weak ring of diameter 12.8 mm. The diffuse band is due to amorphous material which the authors have not identified, and the very weak ring is not found in other similar patterns. In view of the fact that the crystals examined by electron diffraction possessed considerable preferential orientation, while those examined by x-rays were randomly oriented, the absence from the electron pattern of the reflection corresponding to 6.2 Å. is not surprising.

Some of the dry powdered aluminum alpha-monohydrate, supplied by Dr. Frary, was ground in a mortar to make the particles extremely fine. This was dusted upon a well-polished chromium block, and a beam of electrons scattered from the surface at grazing incidence, yielding the diffraction pattern of Figure 6. In Table III are given measured radii and estimated intensities of rings of this pattern, and the corresponding crystal spacings calculated from the relation $d = 2.345 \times 10^{-6}/R$ mm. These spacings and intensities are copied in the sixth and seventh columns of Table I.

It is clear that there is almost perfect agreement between x-ray and electron patterns from the powdered aluminum alpha-monohydrate, and that these patterns differ from those from the authors' layers formed on silica films only in the absence from the latter of reflections corresponding to 6.2 Å. The material giving rise to the electron diffraction patterns of Figures 1 to 5 can be considered as definitely identified as aluminum alpha-monohydrate (boehmite).

As further matters bearing upon this identification, we need to account for the absence from the patterns of Figures 1 to 5 of the reflection corresponding to 6.2 Å. and to report the result of a spectroscopic examination of the film formed upon the surface of massive silica as a result of the reaction of aluminum and water at 38° C. The first of these matters, accounting for the absence of the 6.2 Å. reflection, is taken up below.

For the spectroscopic examination, a rod of fused quartz was soaked for some time in water at 38° C. containing aluminum powder. This rod was dried and brushed thoroughly to remove any loose material from its surface. A very small amount of material could then be scraped from the rod, and this was tested spectroscopically for aluminum and for silicon. Although the analysis showed traces of silicon, it was found that the amount of aluminum present was more than 200 times greater than the amount of silicon. This test proves that the film formed on the surface of the fused quartz rod was a compound containing aluminum but not silicon, in agreement with electron diffraction examinations of the material formed on the surface of amorphous silica films.

Structural Characteristics of Monohydrate Layers

Thickness and Crystalline Orientation. The considerable crystalline orientation indicated by some of the diffraction patterns of Figures 1 to 5 is one of the most striking features of these patterns. The nature of the orientation is the same in all the monohydrate layers studied but its degree varies from zero to perfection, depending upon thickness of the layer and upon other factors.

The film that produced the diffraction pattern of Figure 2 at normal incidence gave a pattern at 45° incidence which is not reproduced here because it appears to be identical with Figure 2. The continuous circles of these patterns prove that the crystals were randomly oriented with respect to the film normal and with respect to a direction at 45° to it, and, since the film normal was the only unique direction, there must have been no preferential orientation of crystals at all.

The symmetry of Figures 1-*A*, 3, 4-*A*, and 5-*A* proves that in each of the corresponding films the crystals were randomly oriented about the normal to the film surface, but about other directions the orientation was not random. Thus in each case the crystals tended to lie with some particular crystallographic plane parallel to the film surface, but were otherwise oriented entirely at random. If this orientation with a particular plane parallel to the surface were approximately perfect the diffraction patterns would differ from those of Figures 1, 4, and 5 in two obvious ways: The patterns at 45° would consist of sharply defined arcs, not lying upon weaker continuous circles; and in the patterns at normal incidence circles would appear corresponding to only those planes which belong to the zone defined by the normal to the film—that is, circles having the same diameters as the arcs along the vertical center lines in the patterns at 45°. These conditions are fulfilled for the pattern of Figure 3 and for one at 45° from the same film which is not reproduced; thus the orientation of crystals in this film was approximately perfect. In the other films, orientation, although marked, was extremely imperfect.

Table III. Data from Electron Pattern of Aluminum Alpha-Monohydrate

(Figure 6)

Measured Radii *Mm.*	Estimated Intensities	Crystal Spacings *Å.*
3.7	4	6.3
7.3	7	3.21
10.0	6	2.34
11.5	1	2.04
12.5	7	1.88
13.1	2	1.79
14.0	3	1.67
15.1	1	1.55
16.2	5	1.45
16.8	1	1.40
17.8	5	1.32
20.0	2	1.172
20.6	3	1.155
22.5	2	1.042
25.8	3	0.909
27.1	2	0.856
28.2	3	0.832
29.2	1	0.803
30.3	1	0.774
35.2	1	0.666
38.2	1	0.614

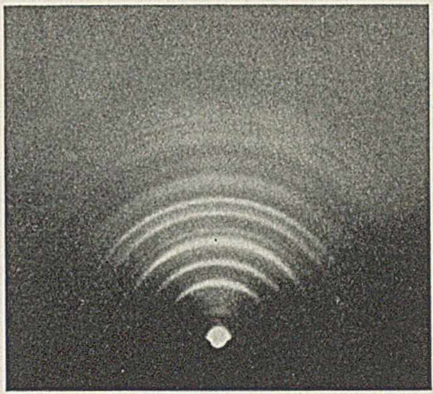


Figure 6. Diffraction Pattern from Powdered Aluminum Alpha-Monohydrate by Reflection Method

A film of silica treated with aluminum and water at 38° for a relatively short period of time (4 hours) gave a diffraction pattern essentially like that of Figure 3, indicating an unusually thin layer of monohydrate made up of perfectly oriented crystals. In monohydrate films deposited upon Formvar from peptized solution it has been found that crystals in very thin layers are almost perfectly oriented, in thick layers imperfectly, and in very thick layers random orientation has been found. There are, however, other factors beside thickness which influence degree of orientation, and these are not understood.

All the crystal planes which tend to lie normal to the film surface in the oriented layers, and which give reflections of observable intensity, have spacings which are inversely proportional to the square roots of the whole numbers 3, 5, 8, 12, and 20. These planes, designated by the numbers in the last column of Table I, were identified by the fact that in the patterns at 45° incidence reflections from them occur as arcs across the vertical center lines. The fact that these important planes, which belong to a common zone, have spacings related in this simple way may give a clue to the corresponding crystal structure, but the authors have not been able to follow it up.

Sizes and Shapes of Crystals. The major part of the widths of diffraction rings exhibited here is due to imperfect resolving power of the individual crystals, presumably on account of their limited size. That part of ring width at half maximum attributable to this cause, ΔR, is related to the mean dimensions of contributing crystals normal to the primary beam, C, by the well-known Scherrer formula which, for the present experiments, can be written $C = L\lambda/\Delta R = 2.3 \times 10^{-6}/\Delta R$ mm. This relation enables one to obtain information regarding mean size and shape of monohydrate crystals in many of the layers.

A surprising feature of Figure 1-*A*, is the fact that the rings corresponding to the whole numbers 3, 5, 8, and 12 are narrower and better defined than other rings. The authors believe that this must be attributed to lamellar shape of the crystals; the two sorts of rings are accounted for if each crystal, irrespective of its orientation, is thin in the direction of the zone axis of its "3, 5, 8, 12 planes" and relatively wide in directions at right angles to this axis. Although microphotometer curves of diffraction rings are necessary for reliable estimates of values of ΔR, experience with a great many such curves (*3*) enables us to make fair estimates visually, and such visual estimates have been made for rings of Figure 1-*A*. These lead to 100 Å. as the average dimension of crystals in directions normal to the zone axis of its "3, 5, 8, 12" planes, and to 30 Å. as the average dimension in the direction of this axis.

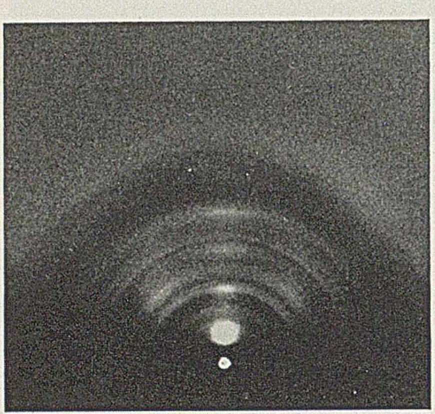


Figure 7. Diffraction Pattern from Aluminum Hydrate Precipitated upon Chromium Block

Extremely thin layers of monohydrate (for example, the layer which produced the pattern of Figure 3) give, in general, patterns at normal incidence showing only the "3, 5, 8, 12 rings", and patterns at 45° incidence showing only short arcs having the diameters of these rings. From the shortness of these arcs in patterns at 45° incidence one can conclude that in these extremely thin layers the orientation is almost perfect, and from the absence of other arcs that the crystals are so thin normal to the film surface that they can scarcely be considered three-dimensional crystals at all.

The observations in this section, and in that immediately preceding, offer a fairly clear picture of the sizes, shapes, and orientations of monohydrate crystals in layers of various thicknesses. In very thin layers (probably less than 20 Å. or 30 Å.) the crystals are usually lamellar in shape, extremely thin, and lie almost perfectly flat upon a supporting silica or Formvar surface. In thicker layers the crystals are still lamellar in shape although not so extremely thin, and are more imperfectly oriented. In addition to thickness, some unknown factors influence shape and orientation of monohydrate crystals; crystals are sometimes randomly oriented, even in layers which are not extremely thick, and sometimes they are not lamellar in shape—for example, the layer which produced the pattern of Figure 2. These deductions regarding size, shape, and orientation of alpha-monohydrate crystals in layers of various thicknesses are consistent with facts already known about the crystallization of gelatinous aluminum hydrate, and they may be of interest in the chemistry of aluminum.

Anomalies in Diffraction Patterns

Missing Reflection Corresponding to 6.2 Å. The degree of orientation in the monohydrate layers which produced the patterns of Figures 1, 4, and 5 was so great that one would not expect reflections from the planes which tend to lie parallel to the film surface, even in patterns at 45° incidence. In other words, on account of crystal orientation the patterns of Figures 1-*A*, 4-*A*, and 5-*A*, must fail to contain reflections from at least one very important set of crystal planes, that normal to the "3, 5, 8, 12" zone axis. Yet all important reflections which appear on x-ray patterns from randomly oriented crystals are present in electron patterns at normal incidence, with the single exception of the reflection corresponding to 6.2 Å. If, then, the identification of aluminum alpha-monohydrate is correct, it is almost certain that the planes which tend to lie parallel to the film surface, normal to the "3, 5, 8, 12" zone axis, are separated by distances of 6.2 Å. The absence of reflections corresponding to 6.2 Å. seems thus to be accounted for on the basis of orientation.

This explanation is, however, inadequate. The crystals which produced the pattern of Figure 2 are known to be randomly oriented, but the pattern contains no ring corresponding to 6.2 Å., or any other ring not a part of patterns from oriented crystals. This is also true of other patterns from randomly oriented crystals. For example, an attempt was made to orient monohydrate crystals favorably for observation of the reflection corresponding to 6.2 Å. by submersion of a polished copper block for 24 hours in water containing aluminum powder at 38° C. The desired orientation of monohydrate crystals was not achieved, as a diffraction pattern obtained from this block by the reflection method was found to be characteristic of randomly oriented crystals of alpha-monohydrate. In this pattern, as in others from monohydrate layers prepared by adsorption from aluminum and water, no trace can be found of the reflection corresponding to 6.2 Å.

The anomaly of this missing reflection is not without precedent. Mongan (*6*) has reported that electron diffraction photographs from graphite powder do not contain reflections from the (002) basal plane which are the strongest reflections in x-ray patterns from graphite, and Trendelenburg (*7*) has found that graphite and a number of compounds which have structures of the layer lattice type often give electron patterns which do not contain reflections from the important basal planes. They attribute the absence of these reflections to lamellar shape of the crystals, which may perhaps be so broad parallel to the basal plane that electrons cannot go through them in this direction. It seems probable that a similar explanation must account also for the absence of reflections corresponding to 6.2 Å. from the monohydrate crystals, which are known likewise to have lamellar shapes in most cases. It is interesting to note again that the aluminum alpha-monohydrate powder, after grinding in a mortar, gave a diffraction pattern, Figure 6, in which a reflection corresponding to 6.3 Å. is clearly observed, although perhaps somewhat weak. We must conclude that grinding does not produce lamellar crystals, at least not such flat ones as are formed by precipitation from aluminum and water.

Diffraction Features Not Due to Alpha-Monohydrate. In a further attempt to orient monohydrate crystals upon a massive block some of the authors' peptized solution of hydrated oxide was used. This was precipitated upon a block of highly polished chromium, and the diffraction pattern of Figure 7 obtained from it by the reflection method. There is no clear indication on this pattern of spots or rings corresponding to 6.2 Å., the diffuse spots along the horizontal center line corresponding not to 6.2 Å., as might have been expected, but to 4.8 Å. This agrees (Table II) with the strongest diffraction ring from beta-trihydrate (bayerite) or from alpha-trihydrate (hydrargillite). Some of the other features of Figure 7 seem to be due to alpha-monohydrate, but many of them are not; all of the latter can be assigned satisfactorily to beta-trihydrate, although the data are by no means adequate to make the identification certain.

It is clear that layers of material precipitated from the peptized solution are, under some conditions at least, not entirely alpha-monohydrate. This has been observed in layers examined by the transmission method as well as those examined by reflection. For example, there are two diffraction rings on Figure 4-*A*, which cannot be assigned to alpha-monohydrate. These are a weak ring of diameter 9.5 mm. and a strong ring of diameter 11.0 mm., corresponding to 4.9 Å. and to 4.3 Å., respectively. The experiment described in the preceding paragraph and examination of Table II indicate that these may well be produced by a small amount of aluminum beta-trihydrate (or alpha-trihydrate). There is, however, no indication of the presence of trihydrate crystals in any of the patterns obtained, either by the reflection method or by the transmission method, from layers formed directly from metallic aluminum and water.

INTENSITY ANOMALIES. On account of the different degrees of orientation in various alpha-monohydrate layers one anticipates different relative intensities of rings. One does, however, expect to find that the relative intensities of rings due to planes of the "3, 5, 8, 12" zone will be the same in all patterns at normal incidence. Yet this is not true. It is obvious on the reproductions that these particular rings stand in order of relative intensity, from strong to weak, 3, 5, 8 in Figures 1-*A* and 5-*A*, but in the order 5, 3, 8 in Figures 3 and 4-*A*. How this can come about is not clear, but exactly the same phenomenon has been reported previously (*4*) in patterns from films of nickel hydroxide, $Ni(OH)_2$.

Miscellaneous Observations

EXPERIMENTS IN BAKELITE BEAKERS. Silica films are often greatly weakened or broken up by treatment with aluminum and water at 38° C. All the tests described thus far were carried out in paraffin-lined glass beakers. When similar tests were attempted in Bakelite beakers the rate of destruction of silica films was greatly increased, and no satisfactory experiments could be made. This destruction of films, which puzzled the authors for some time, was finally explained as due to the mechanical action of bubbles; these are produced by the reaction of aluminum and water, rise to the surface, and break floating films by striking them from below. In a paraffin-lined beaker most of the bubbles adhere to the surface of the paraffin and do not rise to the surface at all, but in a Bakelite beaker all bubbles rise. When a platinum baffle was placed in a Bakelite beaker in such a way that it protected a floating film from rising bubbles, the film lasted longer than in a paraffin-lined beaker without a baffle.

The authors succeeded in obtaining interesting diffraction patterns from silica films treated with aluminum and water in Bakelite beakers only when the films were protected from bombardment by bubbles. The patterns from these films are due to aluminum alpha-monohydrate. The rate of formation of aluminum hydrate on a silica film is, however, many times lower in a Bakelite beaker than under the same conditions in a paraffin-lined glass beaker. Dr. Frary has pointed out that this difference is probably due to adsorption of aluminum hydrate upon Bakelite surfaces but not upon paraffin surfaces, and consequent reduction of the concentration in Bakelite beakers but not in paraffin beakers.

FORMATION OF SCUM. Scum forms on water surfaces in beakers containing aluminum and water at 38° C. This scum develops much more rapidly in paraffin-lined beakers than in Bakelite beakers, and of course it does not develop at all in beakers containing silica and water without aluminum. The difference in the rate of formation of scum in paraffin and in Bakelite is consistent with the observation above, that aluminum hydrate is precipitated upon silica much more rapidly in a paraffin beaker than in a Bakelite beaker, and the difference appears to be accounted for by Dr. Frary's explanation. It seems clear that in the case of long reaction times, during which a great deal of hydrated alumina is formed, much of it appears as scum in a paraffin-lined beaker, but in a Bakelite beaker most of it adheres to Bakelite surfaces.

Many bits of scum have been caught upon Formvar foils for examination by electron diffraction. Scum from Bakelite beakers gives patterns which are readily identified as due to aluminum alpha-monohydrate. Some samples of scum from paraffin-lined beakers also give patterns identified as alpha-monohydrate, but others give patterns which are entirely different. A typical diffraction pattern of the latter sort is reproduced as Figure 8.

The patterns of Figure 9 were obtained under unusual conditions. A small piece of silica and a bit of scum were caught together upon a Formvar foil lying across the usual supporting slit. In the diffraction camera the electron beam could be adjusted so that it passed through the silica or through the scum; the former produced the pattern of Figure 9-*A*, and the latter that of Figure 9-*B*, which were recorded on the same photographic plate. The pattern from the silica film is clearly that of sharply oriented alpha-monohydrate crystals, while the pattern from the adjacent scum resembles that of Figure 8.

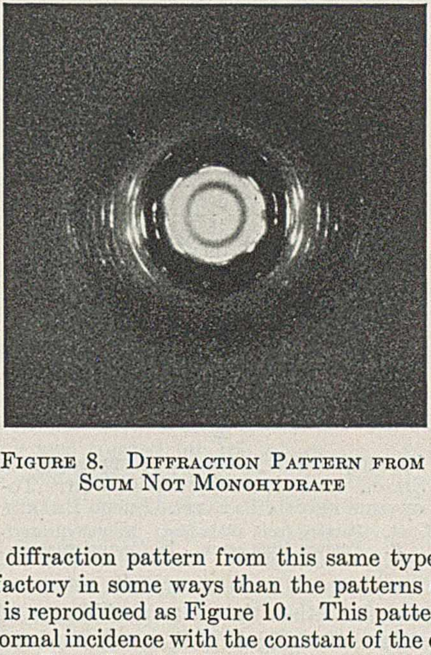
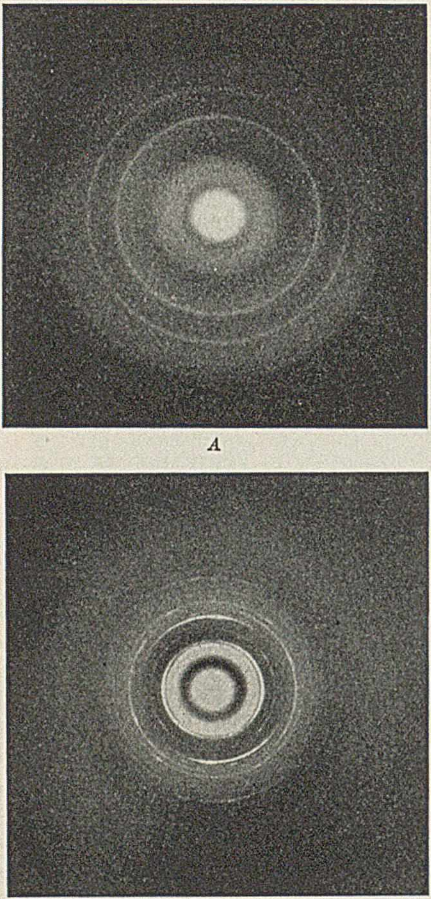


FIGURE 8. DIFFRACTION PATTERN FROM SCUM NOT MONOHYDRATE

Another diffraction pattern from this same type of scum, more satisfactory in some ways than the patterns of Figures 8 and 9-*B*, is reproduced as Figure 10. This pattern was obtained at normal incidence with the constant of the diffraction camera, $L\lambda$, adjusted to 3.205×10^{-6} sq. mm., whereas all other patterns which appear in this paper were obtained at $L\lambda = 2.345 \times 10^{-6}$ sq. mm.

A clue to the structure of this type of scum is furnished by a rectangular array of diffraction spots which can be seen plainly in Figure 9-*B*, and less clearly in Figure 8. Whereas the material which produced the pattern of Figure 10 was polycrystalline, a considerable part of that giving the pattern of Figure 9-*B* (or Figure 8) made up a single crystal. The fundamental rectangle of the arrays of spots in Figures 8 and 9-*B*, has sides of approximately 6.3 and 9.4 mm. Because of change in the constant of the camera a corresponding rectangle in Figure 10 would have sides equal to 6.3 (3.205)/2.345 = 8.6 mm. and 9.4 (3.205)/2.345 = 12.8 mm. It seems probable that the continuous rings of Figure 10 are generated by rotation of such a rectangular array of spots about the direction of the primary beam, and this is proved to be true by data relating to Figure 10 given in Table IV. In the first two columns are given measured diameters and estimated intensities of the rings of Figure 10, and in the last column all possible diameters up to 66.7 mm. as calculated from the relation $D = (73h^2 + 164k^2)^{1/2}$ where h and k are any whole numbers. (In this expression 73 is approximately the square of 8.6, and 164 the square of 12.8.) The agreement between measured and calculated diameters is extremely good.


A

B

Figure 9. Diffraction Patterns from Silica and from Scum Caught Together from a Paraffin-Lined Beaker

A. Pattern from silica film. Monohydrate
B. Pattern from scum. Not monohydrate

It is easy to show that the pattern of Figure 10, and also that of Figure 8 and of Figure 9-*B*, are due to crystals which are sharply oriented each with two of its crystal axes in the plane of the surface.

Table IV. Pattern from Scum Reproduced as Figure 10

Measured		Calculated		
Diameters	Intensities	Miller indices h	Miller indices k	Diameters, $\sqrt{73h^2 + 164k^2}$
Mm.				*Mm.*
..	..	1	0	8.5
..	..	0	1	12.8
15.5	10	1	1	15.4
17.1	9	2	0	17.1
21.4	5	2	1	21.4
25.5	6	0	2	25.6
..	..	3	0	25.6
27.0	3	1	2	27.0
28.6	8	3	1	28.7
30.8	6	2	2	30.8
34.0	5	4	0	34.2
36.3	5	3	2	36.3
		4	1	36.5
..	..	0	3	38.4
39.2	3	1	3	39.4
42.2	3	2	3	42.1
42.8	3	4	2	42.7
..	..	5	0	42.7
44.5	2	5	1	44.6
46.2	1	3	3	46.2
49.7	2	5	2	49.8
51.5	2	0	4	51.2
		6	0	51.3
		4	3	51.4
		1	4	51.9
..	..	6	1	52.8
54.0	1−	2	4	54.0
57.3	2	3	4	57.3
		6	2	57.3
		5	3	57.5
..	..	7	0	59.8
61.2	1−	7	1	61.2
..	..	4	4	61.6
..	..	0	5	64.0
64.0	1−	6	3	64.1
..	..	1	5	64.6
..	..	7	2	65.1
..	..	2	5	66.3
66.8	1−	5	4	66.7

The lengths of the edges of the unit cell parallel to these axes are $2(3.205 \times 10^{-6})/\sqrt{73} = 7.5 \times 10^{-7}$ mm. = 7.5 Å. and $2(3.205 \times 10^{-6})/\sqrt{164} = 5.0 \times 10^{-7}$ mm. = 5.0 Å. (*5*). The product of these two lengths, 37.5 sq. Å., corresponds closely to the known cross-sectional area of two hydrocarbon chains. The complete absence of reflections for which values of the third Miller index can be determined suggests strongly that the length of the unit cell parallel to the third crystal axis is very great. That the structure is probably orthorhombic is indicated by the absence of reflections of the form (*ho*) for h odd, and of (*ok*) for k odd (see Table IV), and, as soon as the presence of long hydrocarbon chains is admitted, by the rather uniform intensity of the rings of Figure 10, and by the fact that the product of the edges $a \times b$ = 37.5 sq. Å. is equal to the known cross-sectional area of two hydrocarbon chains, rather than a larger value which it would have if the structure were monoclinic.

These considerations impel one to the inference that this type of scum is a soap of a long-chain organic acid and, since it does not appear in the absence of aluminum, is an aluminum soap. This conclusion is supported by the pattern of Figure 11 which was obtained at an incident angle of 45° from a sample of scum similar to that which at normal incidence gave the pattern of Figure 10. Except for diffuse rings from the supporting Formvar foil, the pattern of Figure 11 is made up entirely of arcs lying along lines separated by 13.8 mm. and parallel to the axis of rotation. This separation corresponds to a distance of $2.345 \times 10^{-6} \sin 45°/13.8$ mm. = 2.4 Å. repeated normal to the film. The sharpness of the lines proves that this distance is either the length of the unit cell, or is a distance that is repeated many times within each unit cell. As only the latter hypothesis is plausible, the diffraction pattern of Figure 11 offers convincing proof that this type of scum is composed predominantly of long hydrocarbon chains. The difference between 2.4 Å. and the theoretical value of 2.52 Å. is probably attributable to inaccuracy in setting the incident angle of 45°.

Dr. Frary has suggested that the long-chain organic acid, which must be a constituent of this "soap" scum, comes from paraffin, and the authors' observations support this view. In the first place, the soap scum has never been found upon water in a Bakelite beaker. Furthermore, in a paraffin-lined glass beaker only a limited amount of scum is formed. Most of the visible scum was scraped from the beaker from which was obtained the material that gave the pattern of Figure 10, and the beaker was then allowed to stand at 38° C.

for an additional 90 hours; at the end of this time newly formed scum caught from the surface gave an excellent diffraction pattern characteristic of aluminum alpha-monohydrate, without any trace of features attributable to soap. It seems clear from these tests, and from others, that soap scum is formed only in paraffin-lined beakers and only initially, but that monohydrate scum continues to be formed indefinitely, probably as long as aluminum and water are present.

The experiment recorded in the patterns of Figure 9 indicates that, in the presence of monohydrate and of soap, the former is preferentially adsorbed upon silica. Other experiments, which confirm this assumption, are described in the following section.

INFLUENCE OF pH. In the first experiments there was no adjustment of pH of the distilled water which contained aluminum powder, but in later experiments pH was measured roughly and was regulated by the addition of hydrochloric acid or of potassium bicarbonate. Although the number of tests carried out with controlled pH has been undesirably small, some tentative generalizations can be drawn from them.

Scum that has been identified as soap has been obtained from water surfaces in paraffin-lined beakers at pH 4, 7.5, 8.5, and 9. It seems that soap can be formed at any value of pH in this range. Monohydrate scum has been obtained from beakers at high values of pH, but never at low pH. At pH 4 monohydrate scum does not form at 38° C., or, if it does form, the authors have not discovered it.

TABLE V. DATA FROM DIFFRACTION PATTERN AT NORMAL INCIDENCE

(From silica film treated for 160 hours with water containing aluminum hydroxide)

Measured Diameters Mm.	Estimated Intensities (Arbitrary Scale)	Crystal Spacings Å.
11.3	9	4.15[a]
13.2	4	3.55[a]
18.9	1	2.48
21.2	1	2.21
22.7	6	2.06[a]
24.5	1	1.91
26.5	2	1.77
31.1	1	1.51
33.0	1	1.42

[a] Due to planes belonging to zone that tends to lie normal to silica surface.

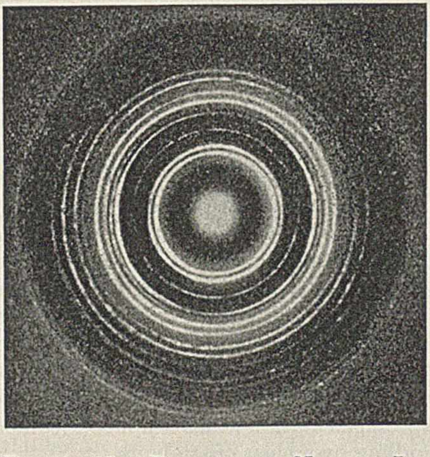


FIGURE 10. PATTERN AT NORMAL INCIDENCE FROM SCUM

$L\lambda = 3.205 \times 10^{-6}$ sq. mm.

At high and medium pH values (6.5 to 9) the material formed on silica films in contact with a mixture of aluminum and water at 38° C. always gives diffraction patterns characteristic of aluminum alpha-monohydrate, without any trace of a pattern which could be attributed to soap. Silica treated with water and aluminum in a paraffin-lined beaker at 38° C. and pH 4 gives results which are quite different. Under these conditions no sharp diffraction pattern is obtained from a silica film in general. In one experiment, after a reaction time of 68 hours at pH 4, a very weak pattern characteristic of soap was obtained from a silica film.

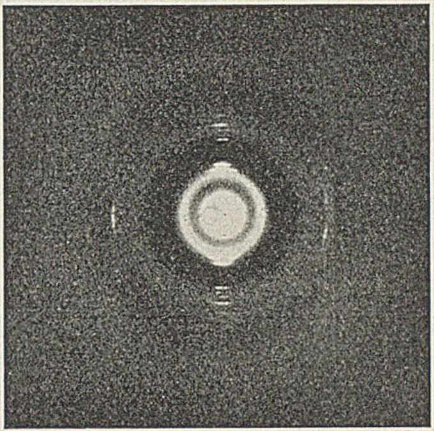


FIGURE 11. PATTERN AT 45° INCIDENCE FROM LAYER OF SCUM

Similar to that which produced Figure 10

$L\lambda = 2.345 \times 10^{-6}$ sq. mm.

These observations can be summarized very briefly. At pH 4 only soap is formed, either as scum or upon silica, but upon silica it seems to form only with extreme slowness and not at all in some cases. At pH 6.5 to 9 only monohydrate is formed upon silica; in this pH range scum is either monohydrate or soap, but usually the former. Soap is not formed upon water surfaces in Bakelite beakers.

EXPERIMENTS WITH COMMERCIAL ALUMINUM HYDROXIDE. Denny, Robson, and Irwin (*1*) have reported that, whereas the solubility of silica in water is greatly reduced by the presence of aluminum powder, it is inappreciably changed by crystalline aluminum alpha-monohydrate or alpha-trihydrate. Because of this observed difference the authors have carried out experiments in which commercial aluminum hydroxide (Eimer & Amend C. P. grade) was used in place of aluminum powder.

Silica films were floated for 65 hours and for 140 hours upon water at 38° C. containing this hydroxide. Diffraction patterns obtained at normal incidence from these films contain sharp rings having the same diameters. The rings from the film which was treated for 160 hours are, however, extremely weak, and those produced by the other film are still weaker. Patterns obtained at incident angles of 45° contain well-defined arcs, proving that the crystals were rather well oriented upon the silica surface. From the extreme weakness of the diffraction features we can conclude that, although some oriented crystalline material was certainly deposited upon these films, the thickness of the layer was a great many times smaller than that of a layer of monohydrate which would have been formed in the same time if metallic aluminum had been used in place of the hydroxide. The failure of aluminum hydroxide (probably hydrargillite) to reduce the solubility of silica in water seems thus to be explained.

In Table V are given data from one of the patterns obtained at normal incidence. It is clear from comparisons of the spacings of the last column of Table V with those given in Table II that the material deposited upon silica in the presence of aluminum hydroxide is not aluminum alpha-monohydrate, alpha-trihydrate, or beta-trihydrate; and that it is not the soap for which data are given in Table IV. Attempts at identification have been made difficult by the extremely weak diffraction patterns available, and have not been successful.

Interpretation

The experiments that have been described prove that the protective film formed on silica as a result of the reaction of aluminum and water is a hydrated oxide of aluminum which after thorough drying in the vacuum of the diffraction camera is crystalline aluminum alpha-monohydrate. Whether or not the film before drying can be properly described as alpha-monohydrate is an uncertainty which the diffraction experiments obviously offer no way of resolving.

There are, however, reasons for believing that the film is probably a highly hydrated gelatinous oxide which becomes crystalline only upon drying. One of these reasons is the fact that Denny, Robson, and Irwin (*1*) have discovered that the protective film formed on silica can be stained a deep pink by aurinetricarboxylic acid; gelatinous aluminum hydrate is stained in this way, but crystalline alpha-monohydrate is not. They observe, furthermore, that activated amorphous alumina (colloidal) is almost as effective in reducing the solubility of silica in water as is metallic aluminum powder, whereas crystalline alpha-monohydrate is almost completely ineffective.

Transformation of amorphous gelatinous hydrated alumina into crystalline alpha-monohydrate upon drying agrees with the known behavior of hydrated oxides of aluminum. Fricke and Hüttig (*2*) state that boehmite (alpha-monohydrate) is the first product of the aging of amorphous aluminum hydroxide gel, being formed from it spontaneously in the cold. The aging of aluminum hydroxide gel at room temperature is said to proceed by way of boehmite and bayerite to hydrargillite. Amorphous gel can be obtained by precipitation from aluminum salt solution only if the operation is carried out rapidly and preferably at low temperature (0° C.). Otherwise a considerable amount of boehmite is obtained.

The authors' experiments have shown that aluminum hydrate is precipitated fairly rapidly upon silica at pH values lying within a range in which lie also the pH values of body fluids of men and of animals. Since in these experiments aluminum hydrate is not precipitated upon silica at pH 4, it seems highly probable that aluminum would not afford protection from silicosis to a hypothetical animal with body fluids of pH 4.

Acknowledgment

The authors are greatly indebted to Dr. Frary for proposing the problem of the identification of the protective film on silica particles, for his continued interest throughout the course of the work, and for a very great amount of assistance and advice over a period of many weeks.

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A Substitute for Laboratory Oil Baths

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THE many difficulties—fumes at high temperatures, spattering from drops of water, messiness from spilling, greasiness on bottoms of flasks, deterioration of oil, etc.—inherent in use of oil baths have prompted replacing them with aluminum pots for air baths. The substitutions have proved such a decided improvement that this mention is warranted.

Special features in construction are (1) thick sides and bottom, which permit drilling thermometer wells in the metal and provide enough heat capacity to keep the temperature reasonably constant for hours at a time; (2) a considerable depth, so that the whole flask and part of the neck can be covered. The depth makes it possible to heat as little or as much of the flask as desired, to cut out a section through which a side arm can protrude so that high-boiling distillates can be kept hot until they reach the receiver, or to use the pots for small furnaces in which short tubes or bottles can be heated. Holes can also be drilled through the bottom or side of a pot as needed for any special furnace construction and subsequently plugged with asbestos without interfering seriously with normal use. The relatively light weight permits suspending many of the pots by their rims in the ordinary iron ring. They can also be supported on their sides or upside down—variations in positions which are sometimes desirable for sublimations, distillations from a horizontal position, or other special operations. Such a degree of usefulness cannot be attained with an oil bath.

It has been found convenient to have pots of different sizes, with about a 3-mm. clearance between the wall and standard-size flasks. This arrangement permits heat to enter through the side of the flask as well as the bottom, so that in distillations there is less tendency for bumping. Asbestos can be placed in the bottoms in order to reduce further the amount of heat from that direction. For molecular distillations with the Hickman alembic or other special apparatus, a closely fitting casting with a slot cut for the low side arm permits a very even heating without necessity of electrical wiring and special insulation which is apt to become loose after repeated handling by a class of students.

The following inside dimensions were found convenient for use with ordinary flasks: 1-liter flask, 14-cm. diameter by 15.5 cm. deep, weight 3.7 kg.; 500-ml. flask, 10.8-cm. diameter by 15.3 cm. deep, weight 2.7 kg.; 300-ml. flask, 9.5-cm. diameter by 19.2 cm. deep, weight 2.9 kg.; 100-ml. flask, 6.9-cm. diameter by 19.6 cm. deep, weight 2 kg.; 50-ml. flask, 5-cm. diameter by 15.4 cm. deep, weight 1.4 kg. Usually the large sizes were made less deep in order to reduce the weight. In all cases the walls and bottom were 1.3 cm. thick. A rim 6 mm. thick and projecting 12 mm. beyond the pot at the top made a convenient grip and support.

Castings were made by S. C. Bockman, 244 Sixth St., Cambridge, Mass.

Tentative Procedures for Testing the Variability of Normal and Concentrated Latex

Crude Rubber Committee, Division of Rubber Chemistry, American Chemical Society, R. H. Gerke, Chairman, U. S. Rubber Products, Inc., Passaic, N. J.

THE committee desires to emphasize that these tentative procedures for testing variability are not to be considered as actual specifications for buying or selling latex, since tolerances or limits are not given. Rather, it is the desire of the committee to give what are believed to be reliable methods for the determination of the various properties of latex which have been listed. However, it may be necessary to revise some of these procedures from time to time, since the use of latex is in its infancy and improved methods are being rapidly developed. In listing these procedures the committee does not mean to suggest that it is always necessary to use all of them in testing a sample of latex. In other words, it is up to the users and suppliers to select such methods and tolerances as they see fit, which will best suit their purposes.

The committee desires to express deep appreciation to those who have been instrumental in preparing the attached procedures:

W. A. Davey, Rubber Research Institute of Malaya
H. E. Elder, Dunlop Tire and Rubber Corporation
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G. A. SACKETT
J. C. WALTON

Sampling Latex[1]

1. LATEX IN DRUMS, L-1a. *Outline.* The contents of the drum are thoroughly mixed and the sample is removed by means of a sample bottle.

Details. In case the sampling operation takes place immediately after the drum is filled, no further mixing is required. In case the drum has stood, the top should be removed and the contents stirred with a high-speed stirrer for 10 minutes.

Attach a 1-liter (32-ounce) open bottle to a 120-cm. (4-foot) length of 0.625-cm. (0.25-inch) steel rod. Introduce the bottle thus attached to the rod into the drum and run it down through the entire body of latex. Withdraw the bottle, discard the contents, refill the bottle, and stopper tightly. This double filling eliminates the possibility of diluting the sample with water which may be present initially in the bottle. It will be found advantageous to leave a small air space in the top of the bottle after the second filling in order to facilitate mixing before weighing out samples.

If closed-head drums are used, a procedure of rolling and up ending the drums must be resorted to. Rolling alone is not sufficient. If there is a free air space in the drum, satisfactory mixing can be accomplished within a short time by this means. In case of full drums, transfer all the latex in the closed-head drum to a larger vessel and then take sample according to either of the above procedures.

2. LATEX IN TANK CARS, L-1b. *Outline.* The contents of the car are thoroughly mixed and a sample is obtained by introducing a 1-liter (1-quart) sample bottle attached to a 300-cm. (10-foot) length of 0.625-cm. (0.25-inch) steel rod.

Details. In case the tank car has been freshly filled, no further mixing will be necessary. If the car has stood, it will be necessary to mix the latex by means of a jet of air from a 1.25-cm. (0.5-inch) pipe inserted through the dome cover of the car and moved continuously throughout the body of the latex. In the case of normal latex, this operation should be continued for 15 minutes, and in the case of creamed or centrifuged latex it should be continued for about 45 minutes.

When the contents of the car have been thoroughly mixed, introduce a 1-liter (32-ounce) narrow-mouthed sample bottle attached to a 300-cm. (10-foot) length of steel rod. Withdraw the bottle and empty the contents back into the car. This initial filling minimizes the possibility of errors from moisture which may be in the bottle. Next, force the bottle quickly down through the body of the latex and raise and lower it rapidly through the entire depth of the tank car several times. On account of the narrow mouth, there will be time to do this during the period of filling of the bottle. Withdraw the bottle when it is completely filled. Pour out just enough latex to leave a small air space in the top and stopper tightly.

Determining Total Solids, L-2

OUTLINE. A weighed sample of latex is dried down for a given length of time under specified conditions of temperature. The film is then weighed and the result of the determination is expressed as percentage of total solids based on the whole original latex.

DETAILS. Weigh out 2.5 ± 0.5 grams of the latex to be tested into a covered tinned ointment can or small covered dish which has been tared. The latex should be uniformly distributed over the bottom of the dish during drying. The area of the latex should be approximately 32 sq. cm. (5 square inches). Remove the cover and dry the sample in air for 16 hours at 70° C. The percentage of total solids may be calculated by means of the following equation:

$$\text{Percentage of total solids} = \frac{100 \times \text{weight of dried film}}{\text{weight of latex sample}}$$

Determining Dry Rubber Content, L-3

OUTLINE. A weighed sample of latex is coagulated with acid, then washed and dried at an elevated temperature. The result is expressed as percentage of dry rubber content based on the whole original latex.

DETAILS. Weigh out into a porcelain evaporating dish a representative sample of not less than 20 grams of normal latex or 10 grams of concentrated latex and add distilled water until the total solids content is approximately 25 per cent. To this add 2.0 per cent acetic acid solution with stirring until the latex appears to be coagulated and more acid produces no effect. Place the dish on a steam bath and leave for 0.5 hour. Pour off the serum and replace with distilled water. Remove the coagulum and pass between the tightly closed rolls of a laundry wringer or similar device; then wash again with distilled water and wring out. Repeat this process five times. Dry the resulting crepe to constant weight at 70° C. Calculate the dry rubber content as follows:

$$\text{Dry rubber content} = \frac{\text{weight of dry coagulum} \times 100}{\text{weight of sample}}$$

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[1] The procedure for sampling latex is given as an example, and may obviously be altered in certain details.

Determining Coagulum, L-4

OUTLINE. A weighed sample of latex is filtered and the coagulum remaining on the filter is washed and dried. The result is expressed as percentage of coagulum based on total solids.

DETAILS. A steel pipe union of about 3.75 cm. (1.5-inch) inside diameter is fitted with a one-hole stopper into a suction flask. Between the two parts of the union, a tared circular section of 80-mesh stainless steel screen is inserted so that when the union is screwed together this screen is held firmly in place.

In order to determine coagulum, weigh out 200 grams of latex from a well-stirred sample and dilute with an equal volume of 5 per cent alkali soft soap solution. Sodium or potassium oleates are recommended. Filter this mixture through the 80-mesh sieve in the steel union and wash the coagulum remaining on the filter with 5 per cent soap solution. Finally wash the coagulum free of soap with distilled water. Remove the screen from the union and dry to constant weight at 70° C. The difference in weight of the screen and the weight of the screen plus coagulum held back represents the weight of dried coagulum. Calculate the percentage of coagulum as follows:

$$\text{Percentage of coagulum} = \frac{10{,}000 \times \text{weight of dried coagulum}}{\text{weight of latex sample} \times \text{percentage of total solids}}$$

Determining Methyl Red Titer or Alkalinity

1. LATEX CONTAINING NO FIXED ALKALI OR BASE OTHER THAN AMMONIA, L-5a. *Outline.* The ammonia in a weighed sample of latex is titrated directly with a standard acid solution, using methyl red as an indicator. The result is expressed as percentage of dry ammonia (NH_3) based on the whole original latex. (The precision of this method is affected by the presence of phosphates and proteins in the latex, which may lead to apparent ammonia contents as much as 0.05 per cent too high based on the weight of the sample.)

Details. Pour approximately 10 cc. of the latex into a tared weighing bottle. Immediately cover the bottle. Weigh it to ±0.05 gram. Place 300 cc. of distilled water in a 600-cc. beaker. Uncover the weighing bottle and immediately immerse it in the water in the beaker. Stir the solution thoroughly with a glass rod. Add 6 drops of a 0.1 per cent alcoholic solution of methyl red and titrate with approximately 0.1 N standard acid until the indicator becomes pink. The end point occurs before complete coagulation takes place and the color change of the indicator can be detected against the white background of the slightly curdy latex. High results will be obtained if the addition of acid is continued until complete coagulation occurs. The calculation is carried out as follows:

Let w = the weight of the sample of the latex
N = the normality of standard acid
n = the number of cc. of standard acid necessary to neutralize the ammonia

$$\text{Then the percentage of ammonia} = 1.7\,\frac{(N \times n)}{(w)}$$

PRECAUTION. In a direct titration of latex with acid, the acid should not be added so rapidly as to produce local coagulation. Continuous stirring and a moderate rate of addition of the acid are recommended to avoid this.

2. PROCEDURE FOR TOTAL AMMONIA CONTENT, L-5b. *Outline.* The ammonia is distilled from a weighed sample of latex, to which has been added an excess of magnesium oxide, into a measured quantity of standard acid. The excess acid is back-titrated with standard alkali solution.

Details. Weigh out 10 cc. of latex, dilute with water to about 250 cc., and add 4 grams of magnesium oxide. From this mixture distill about 100 cc. into 0.1 N sulfuric acid, the amount of the latter exceeding by about 10 cc. the amount used for the determination of the alkalinity. Boil the distillate for 2 minutes and after cooling determine the excess of sulfuric acid by titration with 0.1 N alkali, using methyl red as an indicator.

Determining pH in Latex, L-6

It is recommended that anyone about to undertake the making of measurements of pH without having had previous experience in the use of electrometric apparatus should consult Clark's book (*2*) in order to familiarize himself with the general technique.

OUTLINE. The only suitable means for the accurate determination of pH in latex is the glass electrode.[2] It may be used in conjunction with any one of the various potentiometric arrangements commercially available. In order to make a measurement of pH, the glass electrode is dipped into the solution under test and suitably connected to the reference half-cell and potentiometer. The potentiometer is then balanced, and by means of equations detailed below the potentiometer reading is converted to pH units.

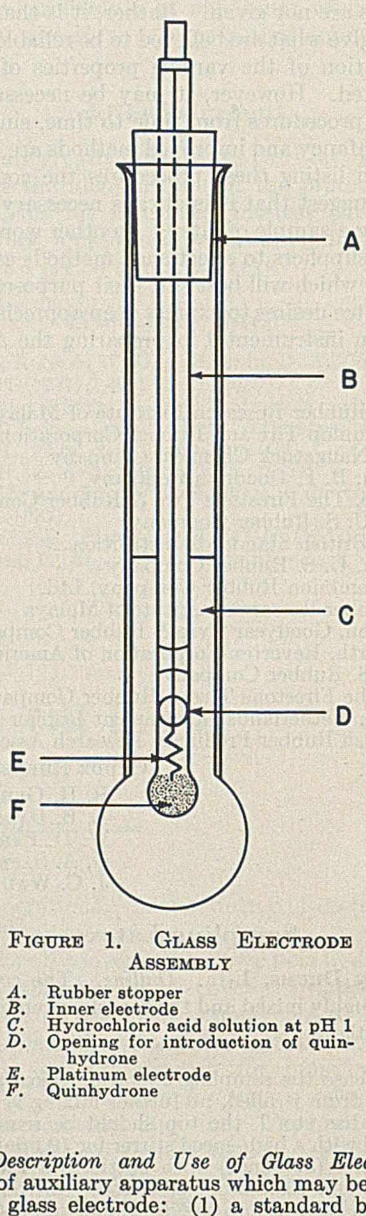

FIGURE 1. GLASS ELECTRODE ASSEMBLY

A. Rubber stopper
B. Inner electrode
C. Hydrochloric acid solution at pH 1
D. Opening for introduction of quinhydrone
E. Platinum electrode
F. Quinhydrone

DETAILS. *Description and Use of Glass Electrode.* There are two types of auxiliary apparatus which may be satisfactorily used with the glass electrode: (1) a standard battery circuit with a student-type potentiometer and a reflecting galvanometer of sufficient sensitivity; (2) a battery circuit with a vacuum-tube galvanometer. Several instruments of the vacuum-tube type are commercially available, some of which require a separate potentiometer and some of which are completely self-contained. For details of preparation and maintenance of glass electrodes and auxiliary apparatus reference must be made to the pamphlets and circulars describing the various individual types of apparatus.

An essential part of the glass electrode is always a thin shell blown on the end of a glass tube of specific composition. This shell contains a standard reference electrode, usually of quinhydrone in a solution of unit pH. When an individual shell has once been prepared for use, it must be calibrated with the help of standard buffer solutions, the pH of which has been determined by means of the hydrogen electrode. When the electrode has been suitably calibrated (detailed directions are to be found below), it is ready for use.

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[2] The reasons for restricting the specification to the use of the glass electrode have been discussed in detail by Jordan, Brass, and Roe (*5*).

In order to measure the pH of an unknown solution, bring the solution to be tested to a temperature of 25° C. or to the operating temperature which prevails in the control test. (A water thermostat kept at this temperature should be available. The calomel reference electrode and the potassium chloride bridge solution should be suitably immersed in this thermostat.) Insert the glass electrode in the test solution so that the bulb is completely immersed, and make the usual electrical connections, including the introduction of a salt bridge between the test solution and the beaker containing the saturated potassium chloride bridge solution, if a separate calomel electrode is used. Balance the potentiometer with respect to the standard cell in accordance with the directions to be found in (*4*) or in the pamphlets of directions provided with special forms of apparatus. When this has been done, replace the standard cell by the glass electrode cell and balance the potentiometer against the latter. The potentiometer reading so obtained may be in terms of volts or directly in pH units depending on the type of apparatus employed. If it is obtained in terms of volts, the reading may be converted into pH units by means of the following equation:

$$\mathrm{pH} = A(E - E_0) \tag{1}$$

where E is the observed potential in volts of the glass electrode-calomel electrode cell as read on the potentiometer, and A and E_0 are constants for any given electrode at a constant temperature.

If the reading is directly in terms of pH units, no such conversion is required, but a calibration curve of the individual electrode should always be obtained and the corrections to scale readings should be utilized in testing unknown samples.

The determination of numerical values for these constants constitutes the calibration of any particular electrode and is described in the next section. When these numerical values are known, pH values may be calculated directly from the potentiometer readings by means of Equation 1.

Calibration of Glass Electrode. Prepare two standard buffer solutions as follows:

1. Add 50 ml. of 1 N potassium hydroxide solution to 50 ml. of 2 N acetic acid solution and make up with distilled water to 500 ml.
2. Dissolve 10 grams of anhydrous potassium bicarbonate in water, add 50 ml. of 1 N potassium hydroxide solution, and make up with distilled water to 500 ml.

It is essential to use potassium hydroxide rather than sodium hydroxide in preparing these buffers, since the glass electrode gives incorrect values in solutions containing sodium ions above a pH of 10. Determine the numerical pH values of solutions 1 and 2 by means of the hydrogen gas electrode in accordance with directions to be found in (*3*). (If sodium hydroxide could be used the hydrogen electrode standardization could be avoided since it is easily possible to obtain carbonate-free sodium hydroxide. However, it is much more difficult to obtain carbonate-free potassium hydroxide, and hence the hydrogen electrode standardization cannot be avoided.) When these buffers have been prepared and standardized, the next step is to find the value of the potential of the glass electrode cell when the glass electrode is immersed in each of the standard buffers.

Let

pH_1 = pH of standard buffer solution 1 as determined by the hydrogen electrode

pH_2 = pH of standard buffer solution 2 as determined by the hydrogen electrode

E_1 = glass electrode potential in standard buffer solution 1

E_2 = glass electrode potential in standard buffer solution 2

Then from Equation 1

$$\begin{aligned} \mathrm{pH}_1 &= A(E_1 - E_0) \\ \mathrm{pH}_2 &= A(E_2 - E_0) \end{aligned} \tag{2}$$

By solution of the simultaneous system 2 in A and E_0, the following results are obtained:

$$A = \frac{\mathrm{pH}_1 - \mathrm{pH}_2}{E_1 - E_2} \tag{3a}$$

$$E_0 = \frac{\mathrm{pH}_1(E_1 - E_2)}{\mathrm{pH}_1 - \mathrm{pH}_2} \tag{3b}$$

If the standard buffer solutions are protected from atmospheric contamination, they will not change in pH appreciably over a period of several months. Hence, the hydrogen electrode standardization need only be repeated at intervals of, say, one month. However, the calibration of the glass electrode should be repeated at frequent intervals; daily, if the glass electrode is in steady use. The aging characteristics of glass electrode shells vary somewhat from shell to shell, and consequently frequent checking of each individual electrode is absolutely essential.

Precautions. On account of the high electrical resistance of the glass electrode and the susceptibility of vacuum-tube galvanometers to external electromagnetic disturbances, special precautions are frequently required to shield the glass electrode outfit from such external disturbances.

If a vacuum-tube galvanometer is used, it has been found advisable to place the water thermostat together with the calomel and glass electrode half-cells within a metal jacket which can be completely closed while the potentiometer is being balanced. This metal jacket and the one side of the potentiometer should be grounded, and the electrical connections to the ungrounded side of the potentiometer should be as short as practicable. If an ordinary battery circuit is used in conjunction with the potentiometer, the galvanometer should be protected from stray sources of e. m. f. by grounding one terminal of the galvanometer and shielding it by means of a moisture-proof box. Frequent testing of the glass electrode in the standard buffers will serve as a check on the presence of external disturbances in the electric circuit. A variation of more than 10 millivolts in the glass electrode potential of either of the standard buffers, provided the buffers themselves have not changed (a point which should be checked with the hydrogen electrode) is an indication of difficulties with the electrical system.

The glass electrode fails in solutions of high pH containing sodium ions; hence, it is impossible to determine pH with the glass electrode in latices stabilized with sodium hydroxide.

When the glass electrode is used in latex, it should always be washed free of latex as soon as the determination is finished; otherwise coagulation may take place on the fragile glass mem-

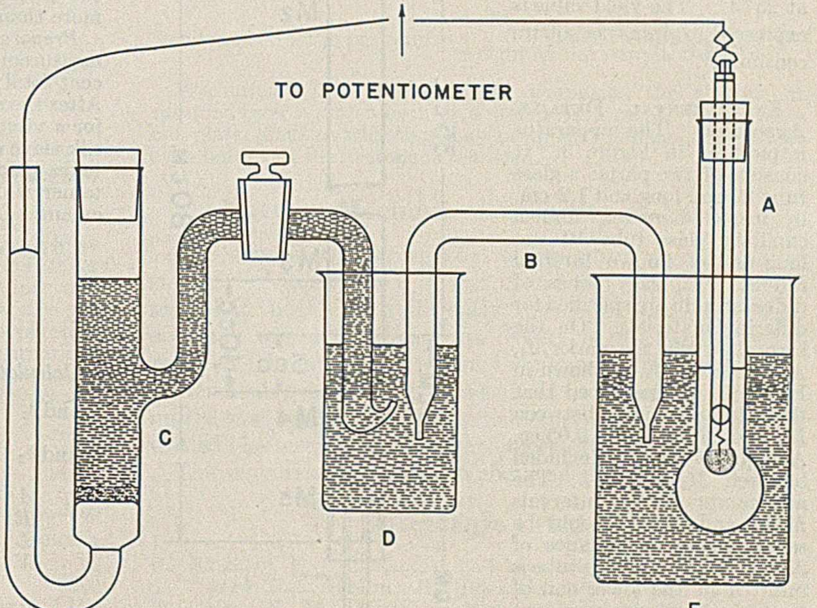

Figure 2. Glass Electrode–Calomel Electrode Assembly for Use with Apparatus Not Completely Self-Contained

A. Glass electrode
B. Agar agar saturated potassium chloride bridge
C. Saturated calomel electrode
D. Beaker containing saturated potassium chloride solution
E. Beaker containing solution under test

brane. In case a light skin of coagulum does form, it may be removed by rubbing the bulb with a soft wet brush.

Determining Viscosity and Yield Point of Latices, L-7

OUTLINE. Two methods have been found satisfactory for the determination of viscosity and yield point of latex—namely, the capillary flow method and the rotating coni-cylindrical viscometer method. The former is advantageous on account of its simplicity and on account of the fact that the apparatus may be constructed from materials stocked in the laboratory. When the capillary viscometer is made in accordance with dimensions hereinafter specified, it is perfectly adapted to the measurement of viscosities of normal and concentrated latex up to 60 per cent total solids. In general, this instrument has the further advantage that results may be obtained in absolute units from a knowledge of the dimensions of the instrument and without recourse to calibration with a liquid of known viscosity. The rotating cylinder viscometer is rather expensive on account of details of its construction. However, this instrument has a wider range of applicability in dealing with latex than is possessed by the capillary flow apparatus and is in addition, from the theoretical point of view, the most satisfactory method of measuring the viscosities of non-Newtonian liquids like latex. In particular, the rotating cylinder viscometer may be used to measure the viscosities of high-solids latex material like Revertex. A description of this instrument is given by Mooney and Ewart (*6*). Specifications will be confined to the capillary flow method.

The capillary flow method consists of measuring the rate of efflux of the liquid to be tested through a capillary tube of known length and known radius under two known pressure heads. The limiting coefficient of viscosity, which is defined explicitly in a later section, is calculated from these data and is expressed in centipoises at 25° C. The yield value is expressed in grams per square centimeter.

EXPERIMENTAL DETAILS. *Apparatus.* The apparatus is pictured in Figure 3. It consists of two parts: a glass tube 80 cm. long and 1.2 cm. in inside diameter, and a capillary glass tube 10 cm. long and of known internal radius. Capillary tubes of different radii are specified for differing materials. On the large glass tube the marks M_1, M_2, M_3, and M_4, as shown in Figure 3, are so placed that the volume included between M_1 and M_2 is 10 ± 0.05 cc. An equal volume is included between M_3 and M_4. The mid-points of the intervals M_1M_2 and M_3M_4 should be separated by a distance of 35 cm. The capillary tube is inserted in the lower end of the 80-cm. cylinder by means of a one-hole stopper. It should be adjusted so that the upper end of the capillary is at a distance of 20 cm. below the mid-point of section M_3M_4 and 55 cm. below the mid-point of section M_1M_2.

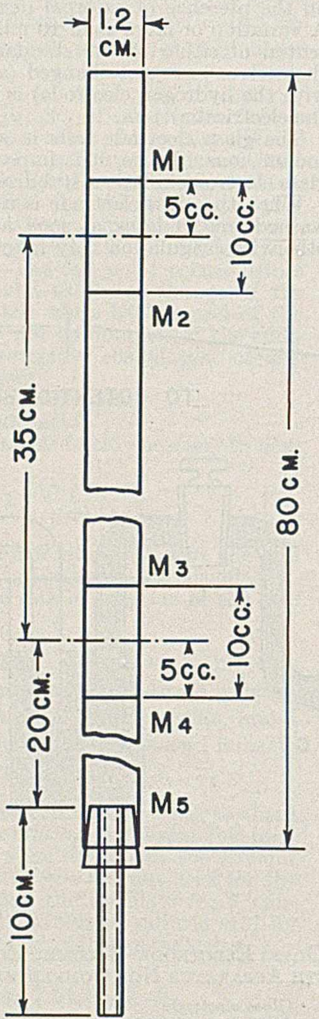

FIGURE 3. VISCOSITY APPARATUS

Procedure for Determining Viscosity and Yield Point. Assemble the glass tubes precisely as shown in Figure 3 and as described in the preceding paragraph. Hold one finger over the lower end of the capillary and fill the tube with latex to a point about 5 cm. above M_1. Place a beaker under the lower end of the capillary and allow the latex to run out through the capillary. By means of a stop watch determine to the nearest tenth of a second the time required for the meniscus to pass through the interval in the 80-cm. tube bounded by marks M_1 and M_2. Similarly determine the time occupied by the meniscus in passing from M_3 to M_4. If difficulty is experienced in seeing the meniscus, a small flash light placed behind the tube will be found helpful. Measure the temperature of the latex to the nearest 0.5° C. just prior to conducting the viscosity determination. During the passage of the meniscus from M_3 to M_4, efflux from the capillary may take place dropwise. This is undesirable and can be prevented by bringing the lower end of the capillary nearly into contact with the latex in the receiving beaker.

Calibration of Capillary. Clean the capillary with chromic acid solution, wash with distilled water, and finally dry; then clamp the capillary in a nearly horizontal position and slowly pipet clean mercury into the upper end until it just flows out at the lower end. Scrape off the protruding meniscus by means of a spatula which is then held tightly against the capillary, and withdraw the pipet so that the capillary is completely filled with mercury. Likewise scrape off the meniscus protruding from the upper end. Empty the mercury contained in the capillary into a weighing bottle and weigh. Duplicate determinations should agree to 0.1 per cent. Determine the length of the capillary by means of a caliper or traveling microscope to the nearest 0.1 cm. Then, if

R = radius of capillary in centimeters
L = length of capillary in centimeters
W = weight of mercury contained when the capillary is full
D = density of mercury at temperature of measurement

the equation giving the radius is

$$R = \sqrt{\frac{W}{\pi LD}}$$

It is of great importance that the capillary be of uniform bore throughout its length. This can be checked up as follows with the aid of a microscope with a traveling stage. Place enough mercury in the clean capillary to fill it about half full. Measure the length of the mercury column in a random position in the tube by means of the microscope. Then tilt the tube so as to shift the position of the column of mercury to another section of the tube, taking care not to lose any mercury, and again measure its length. Repeat this several times. The length of the thread of mercury should not vary from place to place by more than 0.1 per cent.

Preparation of Latex for Viscosity Measurement. All viscosity measurements on concentrated latices should be made at 60 per cent total solids and on normal latices at 35 per cent total solids. After the adjustment of the total solids content, prepare the latex for a viscosity measurement by straining it through a 200-mesh silk sieve and deaerating it overnight. In case partial creaming takes place during the deaeration process, gently swirl the container while the latex is under reduced pressure to stir in this cream. Care should be taken that no bubbles are formed.

Types of Capillary for Use with Normal and Concentrated Latices

Type of Latex	Radius of Capillary Cm.
Normal	0.040 ± 0.002
Concentrated, 60%	0.070 ± 0.004

Calculations. In terms of Figure 3, let

t_1 and t_2 = times in seconds for meniscus to pass through intervals M_1M_2 and M_3M_4, respectively
h_1 and h_2 = heights in centimeters of mid-points of intervals M_1M_2 and M_3M_4, above bottom of capillary
d = density of latex in grams per cc.
R = radius of capillary in centimeters
L = length of capillary in centimeters
V = volume in cc. of each of the two intervals M_1M_2 and M_3M_4
g = acceleration of gravity in centimeters per second per second
T = temperatures in ° C.
η_T = coefficient of viscosity in centipoises at T° C.
η'_T = limiting coefficient of viscosity in centipoises at T° C.
η = coefficient of viscosity in centipoises at 25° C.
η' = limiting coefficient of viscosity in centipoises at 25°C.
F_0 = yield point at T° C. in grams per square centimeter

For purposes of latex testing and control the limiting coefficient of viscosity η' is of more importance than the true coefficient of viscosity, η. In fact, the quantities η' and F_0 completely specify the flow behavior of the latex in the range of practical interest for many purposes. Expressions for the calculation of η' and F_0 are given at this point.

$$\eta'_T = K_1 \frac{t_1 t_2}{t_2 - t_1}$$

where

$$K_1 = \frac{\pi R^4 g\mathrm{d}(h_2 - h_1) \times 100}{8LV} \qquad (1)$$

$$\eta' = \eta'_T \,[1 - 0.02\,(25 - T)] \qquad (2)$$

$$F_0 = K_2 - K_3 \frac{\eta'_T}{t_2} \qquad (3)$$

where

$$K_2 = \frac{h_2 R\mathrm{d}}{2L};\; K_3 = \frac{V}{25\pi R^3 g}$$

Note. The reason for introducing the limiting coefficient of viscosity, η', is that it is a constant for a given liquid of the latex type, whereas the true coefficient of viscosity is not. The introduction of the yield point, F_0, in the present sense and of η' is based upon the treatment of latex as an ideal plastic material in the sense of Bingham. This is not a true picture of the situation, but it is a sufficiently good approximation. A theoretical discussion of the behavior of such plastic bodies in the capillary viscometer is given by Bingham (*1*).

Laying Down Film of Rubber from Latex, L-8

OUTLINE. The purpose of specifying the manner of preparing a dried-down film of latex rubber is to obtain a material which can be directly subjected to the usual procedures for determination of manganese, copper, and acetone extract. A sheet of latex is spread onto a flat horizontal surface and slowly dried down to a transparent film by means of a current of warm air.

DETAILS. Spread the latex to be dried down on a glass plate. Convenient amounts to use will be 1 cc. of normal latex per 6.45 sq. cm. (1 sq. in.) of surface or 0.5 cc. of concentrated latex per 6.45 sq. cm. If the film is to be used to determine acetone extract, carry out the drying process in a current of warm air, the temperature of which should not exceed 35° C. The length of time necessary to complete drying varies with different latices and with external conditions. Experience will indicate safe limits in practice.

It is advisable during the drying process to protect the film from contamination with atmospheric dirt. For this purpose it may be found convenient to use a jet of air which has been filtered through glass wool.

Determining Copper and Manganese, L-9 and L-10

These determinations are carried out on samples of dried-down film in exactly the same manner as directed in the Crude Rubber Committee's specifications for rubber.

Inadvertently the procedures for copper and manganese have not been published. (The abridged reports of the Crude Rubber Committee, which will include the procedures for copper and manganese, will be published shortly in *Rubber Chemistry and Technology.*) The Crude Rubber Committee is cooperating with Sub-Committee XI of Committee D-11 of the American Society for Testing Materials, which has adopted these procedures as tentative but is planning certain revisions at the present time.

Determining Water-Solubles, L-11

OUTLINE. The procedure is to coagulate the ammonia-free latex with dilute acid and then to determine the water-soluble material remaining in the serum.

DETAILS. By means of a weighing pipet, weigh 5 grams of the latex into a 400-cc. beaker and immediately add about 200 cc. of distilled water. Cover with a watch glass and boil on a hot plate until the volume has been reduced by one half. Transfer to a 200-cc. volumetric phosphoric acid flask (this type of flask has a wide neck and is easily cleaned) and make up to within about 200 cc. of the mark. Add 1 cc. of 0.1 per cent methyl orange indicator solution and add 1 *N* sulfuric acid from a buret until the red orange color, indicating a pH of about 4.3, is obtained and the rubber is well coagulated. Too much acid must not be added, as the sample will not coagulate well at an extremely low pH. Shake well to complete coagulation and make up to the mark. Filter the solution and pipet 100 cc. of the clear serum into a weighed evaporating dish. Evaporate to dryness on a steam bath and dry the residue in an air oven at 70° C. to constant weight.

The calculations are made as follows:

$$\text{Weight of solids} = \frac{\text{weight of sample} \times \%\ \text{solids}}{100}$$

$$\text{Weight of water-solubles} = \frac{\begin{array}{c}\text{weight of soluble matter in 100 cc. of}\\ \text{diluted serum} \times (200\text{-weight of solids})\end{array}}{100}$$

From the weight of the total solubles subtract 0.0049 gram for every cubic centimeter of acid used and 0.001 gram for the weight of indicator. Then

$$\%\ \text{water-solubles} = \frac{\text{corrected solubles weight}}{\text{weight of solids}} \times 100$$

The water-soluble matter in latex may be calculated roughly as the difference between the values obtained in the total solids and dry rubber content determinations. When an accurate value for the water-soluble material is not required, it may be calculated by means of this difference. However, in cases where it is important to know the water-soluble material accurately, it will be necessary to resort to the foregoing special procedure.

Determining Acetone Extract, L-12

OUTLINE. A dried-down latex film is extracted for 24 hours with pure acetone. The extract is dried to constant weight and the result expressed as percentage of extract based on the weight of dried film.

DETAILS. Sheet the dried film out as thin as possible on a cold mill (the temperature here should not exceed 40° C.), and use a 2-gram sample for extraction. Extract with freshly distilled acetone for 24 hours in an Underwriter's extraction apparatus. This extraction time will be sufficient for samples 0.0625 cm. (0.025 inch) or less in thickness. Evaporate the extract on a water or steam bath and dry to constant weight at 70° C. It is convenient to use for this purpose a flask which has been previously dried to constant weight at the same temperature. The result may be calculated as follows:

$$\text{Acetone extract in per cent} = \frac{\text{weight of extract}}{\text{weight of film sample used}} \times 100$$

Precaution. It is important to evaporate the acetone as specified over a water bath or a steam bath rather than over a hot plate, since overheating may occur and damage the extract even before all the acetone is removed.

Note on Mechanical Stability of Latex

The committee has omitted a procedure on mechanical stability of latex, since it was considered that the present tests had not been sufficiently developed and that their accuracy was not satisfactory. Work is in progress in the research laboratories of various companies for the purpose of developing a satisfactory test. It is hoped by the committee that suggestions for a satisfactory mechanical stability test will be received from abroad or the United States.

The same remarks apply to chemical stability.

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Reduction by Amalgamated Zinc

Significant Factors in Efficiency

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The rate of reaction between an oxidant and zinc amalgam depends principally on the nature of the oxidant and the concentration of the zinc on the surface of the amalgam. In some cases, reduction is aided by removal of mercury by the oxidant, and in others, the formation of a liquid surface-amalgam takes place.

A large gradation of reduction rates was observed among the compounds examined.

THE amalgamation of zinc which is to be used for reduction in acid solution is a well-known practice. Although its effectiveness in decreasing the rate of reaction between zinc and hydrogen ion is well known, the possibility of a similar decrease in the activity of zinc towards other oxidants appears to have received little, if any, consideration. Recently, an observation of a decrease of zinc amalgam activity in the reduction of chrome alum solutions was reported by Stone and Beeson (*12*), who observed that the reduction by freshly prepared zinc amalgam proceeded rapidly at first, but decreased considerably after some use. It has since been found that by the time 2 per cent of the zinc has been consumed, the reaction becomes too slow to be of any practical value.

An investigation of the causes of this loss of activity has been made by the authors. The results have led to an understanding of the relative importance of various factors in reduction by amalgams, and of the mechanism by which such reduction takes place.

Experimental Methods

In order to compare the relative effects of the various factors on the rate of reduction, a modified Jones reductor was used (Figure 1). The solution to be reduced was placed in the graduated reservoir and slowly forced upward through the amalgam by air pressure. In this upflow type of reductor, advantage is taken of the tendency of the liberated hydrogen to go with the flow of the liquid rather than against it as in the conventional form of the apparatus. Samples of the reduced solutions were measured with the 1-ml. microburet, and the concentrations determined by titration with suitable reagents. To exclude air, the top of the buret was sealed to a bulb filled with inert gas, as recommended by Crowell and Baumbach (*3*). Most of the reduced solution passed up into the bubble trap and out of the capillary regulator, which was inserted to ensure a steady rate of flow. After a run, the volume of hydrogen liberated was measured in an ordinary gas buret.

A standard weight of 20.0 grams of amalgam was used in a reductor of 8-mm. diameter. The solutions to be reduced were prepared 0.2 *N* in both the oxidant and hydrogen ion, unless it is specifically stated otherwise, and were passed through the reductor at rates ranging from 8 to 16 ml. per minute. If the rates of flow through different reductors are compared by calculating the milliliters of solution in contact with unit volume of 20-mesh zinc amalgam, per minute, a rate of 10 ml. per minute in the experimental reductor corresponds to a rate of 225 ml. per minute through a reductor of ordinary size containing about 250 grams of zinc. These comparatively high rates of flow were used to permit effects to be observed more readily. The results were plotted with the percentage reduction as ordinates and the total volume of oxidant passed through the reductor as abscissas.

The following factors were considered of sufficient importance to warrant detailed study: (1) the nature of the oxidant, as determined by the oxidation-reduction potential, the degree of ionization, stability of complexes, tendency to hydrolyze, and similar properties; (2) the degree of amalgamation; (3) the condition of the amalgam due to age, previous use, method of preparation, and manner of storage.

Other factors which were considered but not studied in detail include the temperature, the concentration of the solutions, the acidity, the size of the amalgam particles, and the effect of other ions in the solutions on the oxidation-reduction potentials of the reactants.

Nature of the Oxidant

The position of an oxidant with respect to the mercury-mercurous couple in the oxidation-reduction potential series is a fundamental factor governing its behavior towards zinc amalgams. The stronger oxidants, such as ferric and ceric

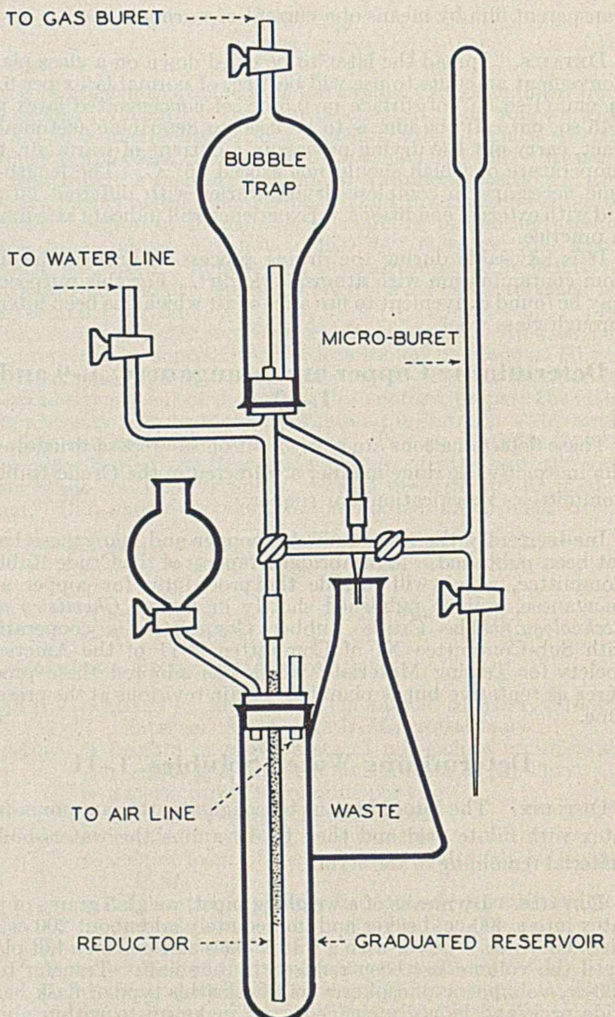

FIGURE 1. DIAGRAM OF APPARATUS

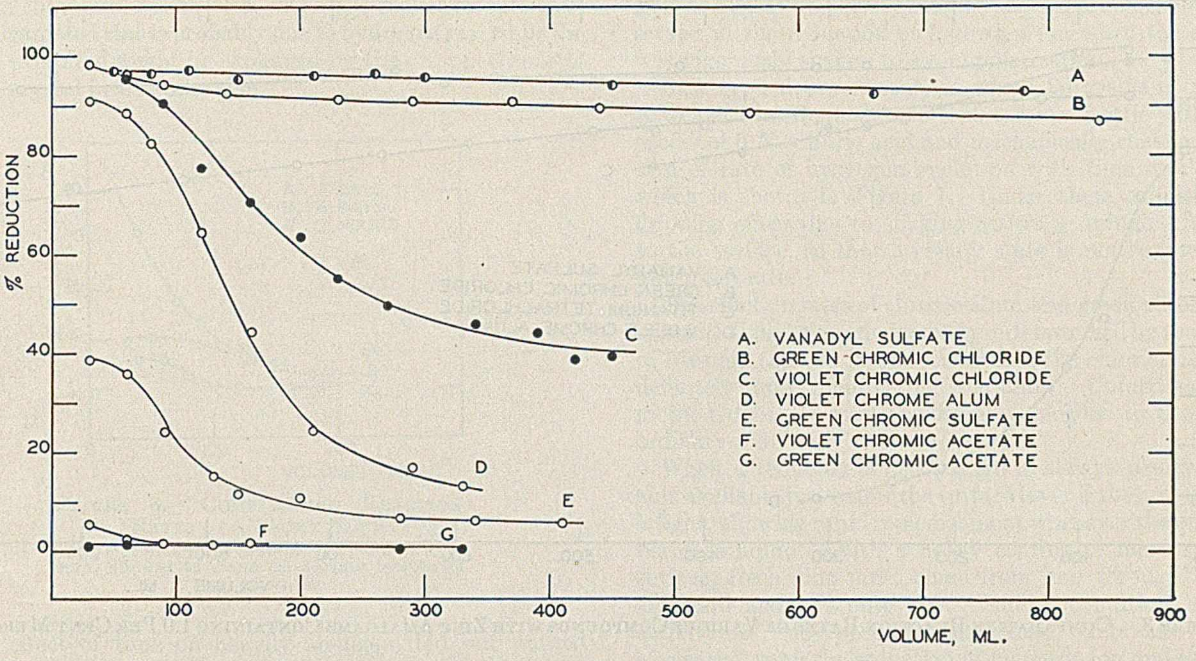

FIGURE 2. COMPARATIVE REACTION RATES OF VARIOUS COMPOUNDS WITH ZINC AMALGAMS CONTAINING 0.01 PER CENT MERCURY

Vanadium reduced, VO^{++} to V^{++}; chromium, Cr^{+++} to Cr^{++}; titanium, Ti^{++++} to Ti^{+++}

ions, may be reduced by either the zinc or the mercury, while the weaker oxidants, such as chromic and titanic ions, must rely on the zinc alone for reduction. The presence of other ions in the solutions containing the oxidants may be significant. Ferric iron in hydrochloric acid solutions is quantitatively reduced by mercury, but in sulfuric acid the reaction reaches equilibrium at about 50 per cent reduction to ferrous (*7*).

The stronger oxidants which were investigated included ferric and ceric sulfates and potassium permanganate. With the standard 20-gram sample of amalgam (1 per cent mercury) and a rate of 10 ml. per minute, the reduction of 0.2 *N* solutions of these oxidants was quantitative and the amalgams showed no deterioration, even with considerable use. In one instance where ferric sulfate was being reduced, the reduction was continued until more than 35 per cent of the zinc had been used without any apparent drop in efficiency.

The behavior of the oxidants not reduced by free mercury is shown in Figures 2 and 3. The compounds reduced were commerical products save the hexaquo chromic chloride and the chromic acetates. The chloride was prepared according to the methods of Werner and Gubser (*14*) and Higley (*6*). The two chromic acetate complexes, which are of doubtful constitution, were the second violet and second green forms of Recoura (*10*), and were prepared according to his directions.

The prominent feature of this group of compounds is the more or less pronounced lowering of the rate of reaction after the amalgam has been in use for some time. The individual differences among the various chromic complexes, for example, were sufficiently characteristic to make the method usable as a qualitative test for identification of the pure salts.

Although contact of the reduced solutions with air was avoided in all cases, the oxygen dissolved in the reagent solutions was not usually removed. In the reduction of chromic salts, this resulted in values which were slightly low because of the rapidity of the reaction between chromous ion and oxygen. By complete removal of the dissolved oxygen from the reagents, 100 per cent reduction was obtained with 0.2 *M* green chromic chloride, even at high rates of flow.

This result is of especial interest in view of the contradictory findings of previous investigators. Traube and Goodson (*13*) made the general statement that violet chromium complexes are more rapidly reduced than green, without having compared the chlorides. Demassieux and Heyrovsky (*4*) in polarographic measurements found that the green chloride is more easily reduced than the violet. Branham (*2*), on the contrary, reported the reduction of green chromic chloride by zinc amalgam to be very slow and to require a large excess of hydrochloric acid. In the present investigation it was found that freshly prepared solutions of green chromic chloride made from the dry salt were rapidly and completely reduced by amalgamated zinc, with or without the addition of acid. The material used was the J. T. Baker Chemical Company C. P. product, which was found on analysis (by precipitation of ionizable chloride with silver nitrate in the cold) to be the dichlorotetraquo complex described in the literature. It was also found that a solution of chromous chloride which had been oxidized by air to chromic (thus forming hydroxo and other basic complexes, *1*) gave a very low reduction rate. Since it is known that chromic chloride standing in the presence of water forms such basic complexes (*11*), many of which are stable to acid, the lack of agreement between different workers may be due to the use of such material.

A plausible explanation for the difference in reduction rates of the violet (hexaquo) chromic chloride and sulfate (chrome alum) lies in the tendency of both the violet chloride and sulfate in solution to form equilibrium mixtures with the green modifications (*5*, *9*). Since the green sulfate reduces very slowly and the green chloride very rapidly, the differences observed are understandable.

When amalgams containing 0.01 per cent of mercury were used, the rate of hydrogen evolution from 0.2 *N* hydrochloric acid was found to fall off in the same manner as the rate of reduction of the green chromic sulfate. The rate of reduction is lessened greatly by the presence of other oxidizing agents,

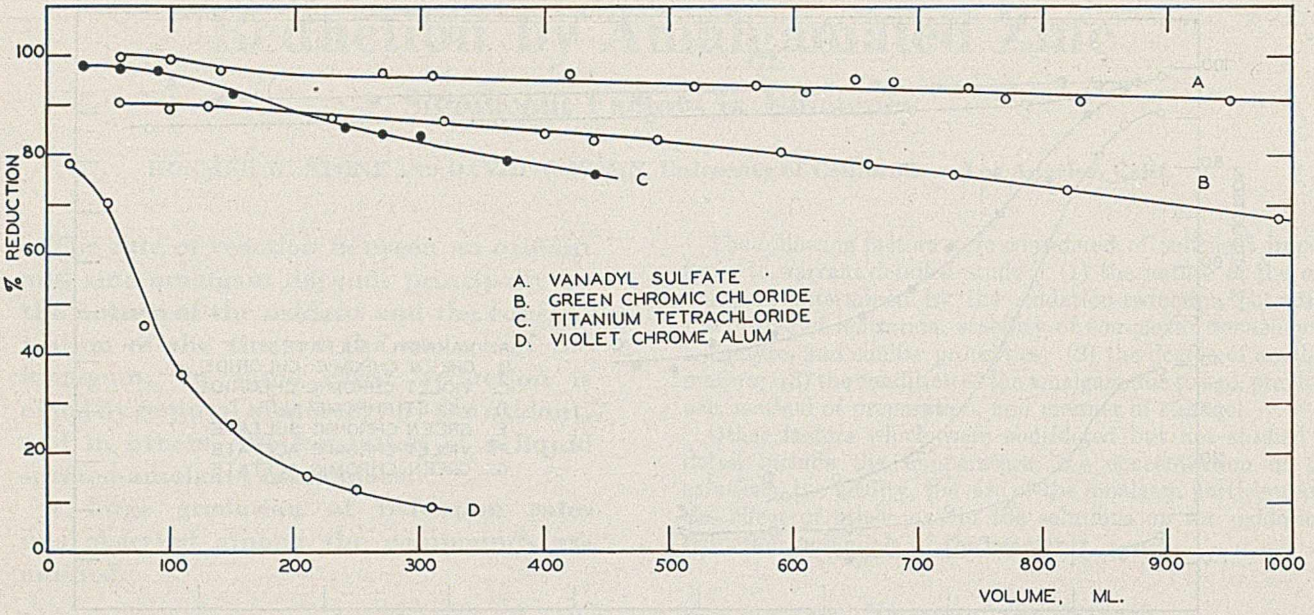

Figure 3. Comparative Reaction Rates of Various Compounds with Zinc Amalgams Containing 1.0 Per Cent Mercury

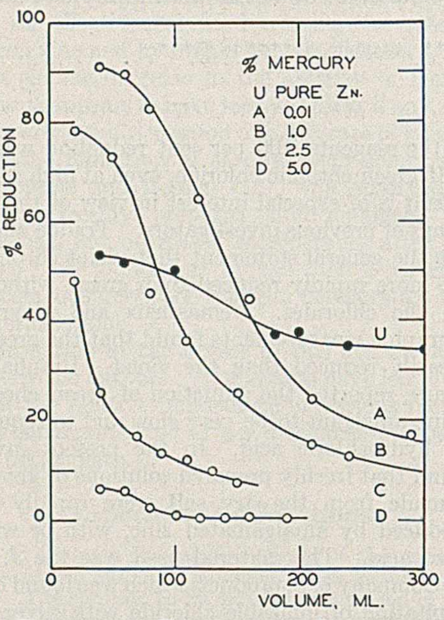

Figure 4. Comparative Reaction Rates of Chrome Alum Solutions

With zinc amalgams containing various proportions of mercury

though only slightly by salt solutions alone. The volume of hydrogen given off in unit time from pure 0.2 *N* hydrochloric or sulfuric acid is approximately double that evolved from chromic chloride or chrome alum dissolved in the corresponding acid. The various oxidants have slightly different effects on the rate of the hydrogen ion–zinc reaction. In the course of long runs with the stronger oxidants, such as ferric iron, the rate of hydrogen evolution would increase markedly.

Degree of Amalgamation

The ideal amalgam should give rapid and complete reduction of the desired substance with minimum liberation of hydrogen. Published directions are often vague and frequently contradictory, the percentages of mercury recommended varying from 0.1 per cent to as much as 10 per cent. During the present investigation, amalgamation was accomplished by washing 20-mesh zinc for 1 minute in sufficient 1 *N* hydrochloric acid to cover it, adding the proper amount of 0.25 *M* mercuric nitrate or chloride, and stirring rapidly for 3 minutes. The solution was then decanted from the amalgam, which was washed and stored under water containing a few drops of hydrochloric acid. Analysis of the decanted liquid and washings showed that within 3 minutes the mercury was 95 to 100 per cent reduced in the preparation of amalgams containing as much as 10 per cent of mercury, indicating that the reaction is very rapid. The chloride and nitrate seem to be equally satisfactory.

The effect of varying the percentage of mercury in the amalgam on the rate of reduction of chrome alum and green chromic chloride is seen in Figures 4 and 5. The solutions were

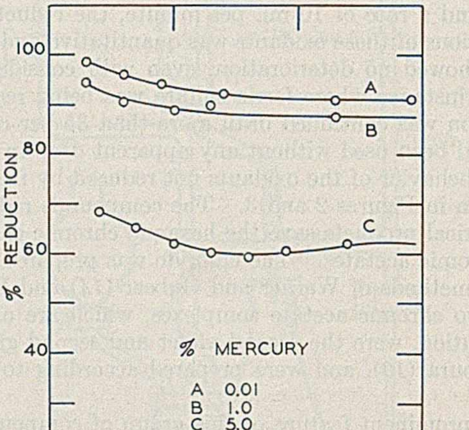

Figure 5. Comparative Reaction Rates of Green Chromic Chloride Solutions

With zinc amalgams containing various proportions of mercury. Flow of solution through reductor in run with 5 per cent amalgam was interrupted for 3 minutes at 170-ml. point

0.2 M in chromium and in acid. The low reduction rate with unamalgamated zinc is probably due to hydrogen gas, while the decline exhibited might be explained by the disappearance of broken crystal faces in the zinc.

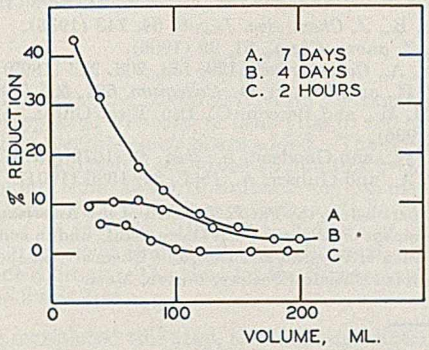

Figure 6. Comparative Reaction Rates of Chrome Alum

With zinc amalgams containing 5 per cent mercury, allowed to stand for various lengths of time before use

The effect of time on heavily amalgamated but unused samples of zinc is shown in Figure 6. As the amalgams are allowed to stand in slightly acid water, they become more active. It was found, however, that lightly amalgamated samples, which were active when fresh, became coated with a white precipitate and lost much of their activity if allowed to become dry in air or even to stand in water exposed to the air for long periods of time.

Surface Effects during Reduction

From the evidence which has been presented, certain conclusions have been drawn. Under the conditions of the experiments, the governing factor in the rate of reduction of a given weak oxidant is the amount of available zinc at the surface of the amalgam, and the depletions which were observed were due to the lowering of the concentration of the zinc in the surface layers. Diffusion of zinc through solid amalgams is very slow, heating being necessary to obtain a rapid revival of activity. Light amalgams were completely restored by heating for an hour in an atmosphere of nitrogen at about 400°. The stronger oxidants were reduced by both the zinc and mercury rapidly enough so that depletion effects did not appear. That mercury is actually removed from portions of the amalgam surface is shown by the increased amounts of hydrogen which were obtained.

The absence of observable depletion effects during the reduction of green chromic chloride and vanadyl sulfate is due to the formation of a liquid amalgam surface, through which the diffusion of fresh zinc is sufficiently rapid to keep pace with the removal by oxidation. This view is supported by a number of facts. During runs with titanic chloride and chrome alum, for example, the particle size was found to remain uniform throughout the reductor. However, with green chromic chloride and vanadyl sulfate, the particles at the entrance of the reductor became greatly reduced in size without any visible change in the others. In one instance, approximately one third of the zinc was dissolved under these conditions.

For a short time after amalgamation, especially with larger amounts of mercury, a definite surface liquidity could be observed. On standing in contact with one another, the particles would set into a single mass which could be crumbled into permanently discrete particles. The same behavior was observed in amalgams which had been used in the reduction of considerable amounts of green chromic chloride. The formation of visible amounts of liquid amalgam could also be observed in the reduction of hydrogen ion when the amalgam was vigorously shaken to avoid polarization.

In a typical experiment, in which 20 grams of amalgam (0.01 per cent mercury) were placed in a bottle with a large excess of 6 N sulfuric acid and mechanically shaken, a variation of rate of hydrogen evolution with time was obtained which is shown in Figure 7. Under these conditions, the grinding effect due to shaking assists in bringing fresh zinc to the surface, so that a steady state is not reached at the minimum rate.

The reaction rates of chrome alum and green chromic chloride with liquid zinc amalgams were determined by the methods of Masuda (*8*) and it was found that the chloride is reduced definitely more rapidly than the alum. Unfortunately, the method does not give conditions analogous to those in the ordinary reductor.

When a reductor is used, there is always plenty of fresh zinc available just below the surface layer if the amalgamation is light, allowing rapid replenishment whenever the outer layer becomes liquid. With a heavy coating of mercury on the surface, fresh zinc must come from and through layers of amalgam and not pure zinc. Similar conditions affect the activity of freshly prepared amalgams. Here, also, the heat of reaction from the reduction of mercuric ion makes possible a more rapid diffusion of zinc to the surface.

Recommendations for Practical Amalgamation

The amount of mercury which it is desirable to deposit on the zinc in practical work is dependent principally on the acidity of the solution, the type of oxidant, the size of the reductor, and the rate at which the solution is to be passed through the reductor.

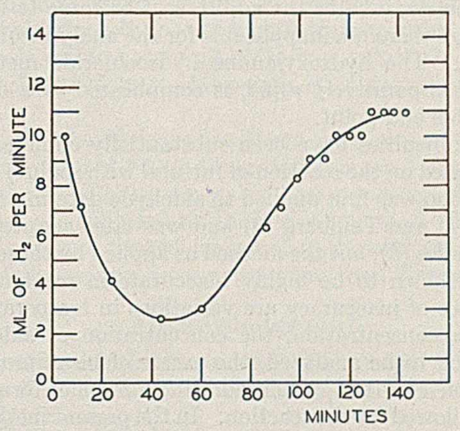

Figure 7. Rate of Evolution of Hydrogen from 6 N Sulfuric Acid

By action of zinc amalgam (0.01 per cent mercury), under vigorous agitation

In working with oxidants which are not reduced by mercury, the least amount of mercury which will enable satisfactory control of hydrogen evolution should be used, since heavy amalgamation tends to reduce the rate of reaction. With acid concentrations of about 0.2 N or less, 0.1 per cent of mercury is satisfactory for oxidants such as chrome alum or vanadyl sulfate, but the use of more than 1 per cent of mercury is likely to result in too slow a reduction rate. For those oxidants which are reduced by mercury as well as by zinc, and particularly at higher acid concentrations, as much as 5 per cent of mercury may be desirable.

The results of this work indicate that with a 2 × 30 cm. reductor charged with 20-mesh amalgamated zinc, the customary rates of flow are in many cases unnecessarily slow. For those oxidants tried which reacted with free mercury, a rate of 200 ml. per minute was not too rapid for complete reduction. The oxidants not reduced by mercury usually require a somewhat lower rate of flow through the reductor, especially after the amalgam has had considerable use. For any given oxidant not studied in this work, it would not be possible to predict the limiting conditions for percentage of mercury and rate of flow. However, a comparison with the types given should indicate something of what might be expected.

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Determination of Furfural in Furfural-Furfuryl Alcohol Solution

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IN THIS laboratory it has been necessary to make a large number of analyses for furfural in solution in furfuryl alcohol. It was desirable to have a simple, rapid method with a reasonable degree of accuracy.

A study of the analytical procedures for the determination of this aldehyde revealed that the phloroglucinol (*1*), thiobarbituric acid (*7*), and 2,4-dinitrophenylhydrazine (*10*) methods, which are gravimetric, are much too slow. The Hughes-Acree (*5*) and Kullgren-Tyden (*8*) methods, which are volumetric, involve the addition of bromine to the furan ring and are therefore inapplicable for the analyses under consideration. The hydroxylamine hydrochloride method (*2*), which is comparatively rapid, is complicated by a difficultly reproducible end point.

These difficulties have been substantially eliminated by a method based on the reaction of furfural with sodium bisulfite. This reaction was first applied to aldehyde determinations by Ripper (*11*) and Feinberg (*3*) and was later adapted to furfural by Jolles (*6*), but the method as applied by these workers has been shown to be highly inaccurate in most cases (*9*). The sources of inaccuracy are variations in temperature, hydrogen-ion concentration, the concentration of aldehyde in the solution to be analyzed, the excess of bisulfite used, the dissociation constant of the addition products formed, and the time allowed for the reaction. In the present method some of these conditions are constant and the use of the proper correction factor compensates for the effect of the others.

Reagents

Approximately 0.1 *N* sodium bisulfite solution is prepared by dissolving 5.2 grams of acid sodium sulfite ($NaHSO_3$) in distilled water and diluting to 1 liter. The effective concentration of this solution is redetermined for each series of analyses by titrating with 0.1 *N* iodine.

The iodine solution is prepared by dissolving 12.6 grams of resublimed iodine and 25 grams of potassium iodide in distilled water and diluting to 1 liter. This iodine solution is restandardized frequently against 0.1 *N* sodium thiosulfate, using starch solution as an indicator.

Preparation of Samples

From a determination of the density or the refractive index or by a rough analysis an estimate is made of the concentration of furfural in the solution to be analyzed.

If the solution contains 0 to 9 per cent of furfural, approximately 10 grams are weighed out and made up to 100 ml. with distilled water in a volumetric flask. If the estimate shows 10 to 100 per cent of furfural a quantity is weighed out such that, when

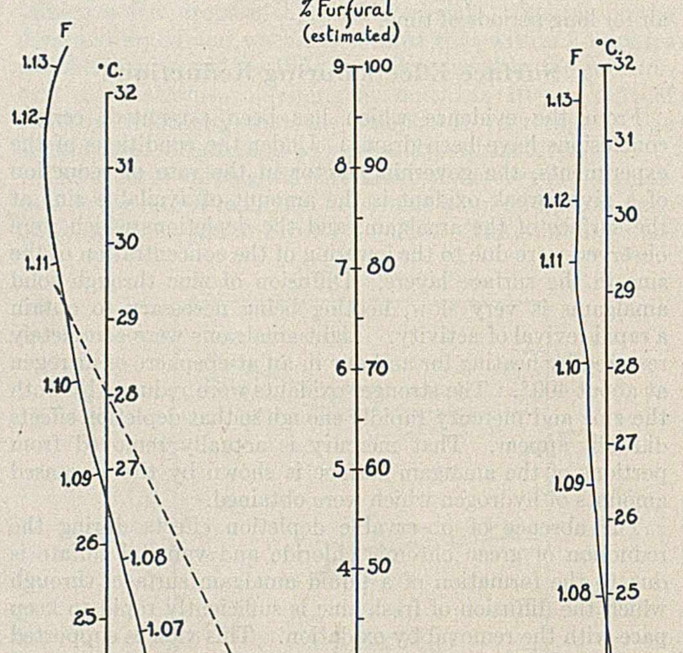

Figure 1. Nomographs

diluted to 100 ml. with distilled water, the resulting solution contains approximately 1 gram of furfural. If the solution for analysis is difficultly soluble in water, ethyl alcohol may be substituted as the solvent. Tests in this laboratory have shown that this substitution has no effect on the amount of iodine required for titration. From this point on, the procedure is exactly the same, regardless of the concentration of furfural in the original solution.

Analysis

Five milliliters of the prepared furfural solution are transferred to a glass-stoppered Erlenmeyer flask (100 to 150 cc.) and 25 ml. of the sodium bisulfite solution are added. The resulting mixture is shaken and allowed to stand for 15 minutes (±1 minute). In the intervening time, 25 ml. of the same sodium bisulfite solution are added to a similar Erlenmeyer flask, and allowed to stand for 15 minutes (±1 minute). Then 3 to 4 drops of starch solution are added to each of the samples which are then titrated with 0.1 *N* iodine solution. The time for the titrations should be kept within 1 to 2 minutes.

Having completed this step, the concentration of furfural in the sample being analyzed is obtained by use of the following equation, where *F* is a correction factor which is determined from the nomographs (Figure 1).

$$\text{Per cent of furfural} = \frac{F(\text{ml. of } 0.1\,N\,I_2\text{ control} - \text{ml. of } 0.1\,N\,I_2\text{ sample}) \times 0.0048 \times 20 \times 100}{\text{weight of sample}}$$

Explanation of Nomographs

The center line of the graph serves a twofold purpose, the left side indicating concentrations of furfural from 0 to 9 per cent and the right indicating concentrations from 10 to 100 per cent. The nomograph on the left side of the page refers to the left side of the concentration line, whereas that on the right refers to the right side of the concentration line. Having estimated the concentration of furfural in the sample to be analyzed, the correction factor, *F*, is determined by laying a straight-edge across the appropriate nomograph from the estimated point on the concentration line to the point representing the room temperature. The intersection of the straight-edge and the factor curve of the nomograph gives *F* to the nearest hundredth.

Data

The furfural and furfuryl alcohol used were prepared from the technical grade of each by fractionating three times under vacuum, discarding approximately 15 per cent of the total volume at the beginning and end of each distillation.

Solutions of these products of known concentration were analyzed by three different laboratories, using the procedure described above.

Sample Calculation

Solution 2 (Table I) was estimated to contain 0.5 per cent of furfural; hence a sample of approximately 10 grams (10.5096 grams) was weighed out and made up to 100-ml. volume with distilled water. The analysis was performed in triplicate at a temperature of 28° C., and the amount of iodine solution required was 21.76, 21.77, and 21.75 ml., respectively. The control solution required 22.69 ml. to the same end point, which is a difference of 0.93 ml. of 0.1025 *N* iodine. *F* was determined by placing a straight-edge on the left-hand nomograph from 0.5 per cent furfural to 28° C., whence *F* was found to be 1.11. The concentration of furfural in the sample was then calculated by substituting these values in the equation shown above.

$$\text{Per cent of furfural} = \frac{1.11 \times 0.93 \times 0.0048 \times 1.025 \times 20 \times 100}{10.5096} = 0.97$$

Comparison with Other Methods

Table II shows the results obtained in analyzing furfural by the thiobarbituric acid, hydroxylamine hydrochloride, and 2,4-dinitrophenylhydrazine methods (*4*), compared with results obtained by the present method. It indicates the comparative accuracy of the methods when analyzing pure furfural.

Table I. Analyses of Furfural in Solution in Furfuryl Alcohol

Solution No.	Furfural Present	Furfural Found			
		Lab. 1	Lab. 2	Lab. 3	Average
	%	%	%	%	%
1	0.00	0.00	0.20	0.10	0.10
2	0.96	0.97	1.32	1.21	1.17
3	1.61	1.61	1.72	1.70	1.68
4	2.11	2.14	2.10	2.18	2.14
5	4.36	4.66	4.66	4.67	4.66
6	5.49	5.44	5.82	5.37	5.54
7	8.78	8.66	8.85	8.68	8.73
8	14.99	15.02	15.44	....	15.23
9	32.98	33.41	33.07	33.40	33.29
10	45.50	45.19	....	....	....
11	62.70	62.61	63.62	62.68	62.97
12	100.00	100.20	101.26	100.80	100.75

Table II. Furfural Found on Analyzing Furfural

Sample No.	Thiobarbituric Acid (*7*)	Hydroxylamine Hydrochloride (*2*)	2,4-Dinitrophenylhydrazine (*10*)	Bisulfite-Iodine
	%	%	%	%
1	103.92	100.52	99.33	100.20
2	102.49	101.63	98.83	101.26
3	103.39	102.35	97.81	100.80
4	104.35	....	98.88	....
5	103.14	....	...	....
6	102.85	....	...	....
7	104.13	....	...	....
Av.	103.47	101.50	98.71	100.75

Discussion

Rapid and reasonably accurate analyses for furfural in solution in furfuryl alcohol may be made by the bisulfite-iodine method when applied as described in this article. When analyzing solutions of high furfural concentration, the accuracy is within 1 per cent of the true value. Larger deviations are found when working with solutions of low furfural content.

The authors' experience has shown that solutions of furfural in furfuryl alcohol on standing undergo some change which affects their solubility in water and produces high results when they are analyzed by the present method. This factor has not been investigated, inasmuch as the solutions for analyses in this laboratory were never more than 2 days old.

Acknowledgment

Acknowledgment is hereby made of the initial development work on this method by J. Pokorny, G. S. Blakeslee and Company, Chicago, Ill.

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Composition of Lithium and Potassium Salts Precipitated by Uranyl Acetate Reagents for Sodium

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THOUGH various investigators have shown that certain uranyl acetate reagents for sodium precipitate lithium also when added to lithium solutions of moderate concentration, considerable uncertainty seems to exist as to the composition of the precipitates so produced. Certain investigators believe that the lithium precipitates are only double acetates of lithium and uranyl, whereas others have concluded that they are triple acetates analogous in composition to those produced by the interaction of these reagents with sodium solutions.

Chamot and Bedient (*4*) state that they were unable to prepare a triple acetate in which lithium replaced sodium, and conclude in general that, of the members of Group I of the periodic system, sodium alone yields a triple uranyl acetate containing magnesium, zinc, cadmium, cobalt, nickel, iron, manganese, or copper. On the other hand, Insley and Glaze (*6*), and later Miller and Travers (*9*), have shown rather conclusively by careful analyses that the precipitate produced by the addition of the zinc uranyl acetate sodium reagent to lithium solutions is a triple acetate analogous in composition to the hexahydrated sodium zinc uranyl acetate produced by the addition of this same reagent to sodium solutions. Moreover, Feldstein and Ward (*5*) found that the precipitate formed by the addition of their nickel uranyl acetate reagent to lithium solutions contained lithium, nickel, and uranium, though apparently no quantitative analysis of this salt was made. No careful analysis appears to have been made of the lithium salt precipitated by any of these sodium reagents other than zinc uranyl acetate.

The information available in the literature concerning the composition of the precipitates produced in potassium solutions of sufficiently high concentration by the uranyl acetate reagents for sodium is likewise incomplete and contradictory. Thus, for example, Kolthoff in one paper (*8*) speaks of the potassium precipitate formed by the zinc type of reagent as potassium uranyl acetate, whereas in another paper (*7*) he calls it the triple salt, potassium zinc uranyl acetate. Barber and Kolthoff (*1*) describe it as potassium zinc uranyl acetate, and Insley and Glaze (*6*) in their study of the crystal form and structure of the salt precipitated from potassium solutions by the zinc uranyl acetate reagent likewise consider it to be this triple salt. On the other hand, Feldstein and Ward (*5*) state that the precipitate produced by the addition of nickel uranyl acetate reagent to potassium solutions is not a triple salt but only the double salt, potassium uranyl acetate.

No quantitative analysis appears to be given anywhere of the precipitate produced in potassium solutions by any type of uranyl acetate sodium reagent. Various views concerning the composition of these precipitates have been repeated by later workers or have been extended by analogy to the composition of precipitates produced by types of reagents other than the two specifically mentioned. Unfortunately this has further increased the confusion concerning the nature of these precipitates. In view of the incomplete and conflicting information concerning the composition of these lithium and potassium precipitates it seemed worth while to investigate their composition critically. This involved the preparation of all the possible general types of uranyl acetate reagents for sodium, including some not previously described, the precipitation of lithium and potassium in various ways by these reagents, and the careful analysis of the precipitates thus obtained. Since any one reagent of a given type, such as magnesium uranyl acetate, for example, was found to yield precipitates of the same composition in spite of minor variations in the formula of the reagent, the only experiments here described are those that were made with a series of reagents prepared according to a similar general formula—the one that is usually followed in the preparation of those uranyl acetate sodium reagents that have come into general use.

Preparation of Reagents

The magnesium uranyl acetate reagent was prepared according to the directions of Caley and Sickman (*3*). The zinc uranyl acetate reagent was prepared in a similar way, except that 200 grams of zinc acetate dihydrate were used in place of the specified quantity of magnesium acetate tetrahydrate. The nickel uranyl acetate reagent was prepared according to the directions given by Feldstein and Ward (*5*). The cobalt, manganese, and cadmium uranyl acetate reagents were prepared like the nickel uranyl acetate reagent except that 200 grams each of cobalt acetate tetrahydrate, manganese acetate tetrahydrate, and cadmium acetate dihydrate, respectively, were used.

Though the ferrous uranyl acetate reagent was prepared according to the same basic formula, the ease with which concentrated ferrous acetate solution oxidizes on contact with air necessitated a special method of preparation. The solution of ferrous acetate was made by dissolving equivalent quantities of barium acetate monohydrate and ferrous sulfate heptahydrate in separate portions of water freed from dissolved oxygen, mixing these two solutions, filtering off the precipitated barium sulfate, and concentrating the resulting solution under reduced pressure. The concentrated ferrous acetate solution was then mixed with a previously prepared solution containing the uranyl acetate and acetic acid. This whole process was carried out with nitrogen gas above the solutions.

In the preparation of the mercuric and copper uranyl acetate reagents, the same quantities of uranyl acetate, acetic acid, and water were used as for the nickel uranyl acetate reagent, but the weights of the divalent acetates taken were of necessity less than 200 grams because of the lower solubilities of these acetates. For the mercuric uranyl acetate reagent 100 grams of the anhydrous salt were used and for the copper uranyl acetate reagent 70 grams of cupric acetate monohydrate. After mixing, all these reagents were maintained at 20° C. for at least an hour before they were filtered into dry containers.

General Experimental Procedure

All precipitations of lithium were made from concentrated lithium acetate solutions prepared by dissolving pure lithium carbonate in concentrated acetic acid. The lithium carbonate was purified, especially for the purpose of eliminating sodium, by the method of recrystallization devised by Caley and Elving (*2*). The volume of reagent used for all precipitations was 100 ml. During precipitation the solutions were stirred mechanically for 1 hour at 20° C., after which the lithium precipitates were filtered off on weighed glass filter crucibles, washed with eight 5-ml. portions of 95 per cent ethyl alcohol, and dried to constant weight, usually at 100° to 105° C. All precipitations of potassium were made from concentrated potassium chloride solutions under the same conditions as to volume of reagent, time allowed for precipitation, and method of filtration and washing. The potassium precipitates were usually dried to constant weight at room temperature. The samples for analysis were then taken from the dried lithium and potassium precipitates.

Composition of Lithium Precipitates

Regardless of rather wide experimental variations in the volume and concentration of the lithium solutions, the salts precipitated from these solutions by all the reagents that formed precipitates were always found to be triple acetates analogous in composition to the triple acetates precipitated from sodium solutions by these same reagents.

Lithium Magnesium Uranyl Acetate. In the first preparation 1.100 grams of lithium carbonate were dissolved in 6 ml. of glacial acetic acid and 4 ml. of water and precipitated with the standard volume of magnesium uranyl acetate reagent. The yield was 3.39 grams. In the second preparation 0.551 gram of lithium carbonate was dissolved in 4.5 ml. of glacial acetic acid and likewise precipitated. The yield was 3.42 grams.

In the analysis of these preparations the uranium was precipitated as ammonium diuranate with carbonate-free ammonium hydroxide and weighed as U_3O_8. The same method for the determination of the uranium was used in the analysis of all the other precipitates. The magnesium was precipitated in the filtrate from the uranium separation with 8-hydroxyquinoline and weighed as the hydroxyquinolate. In the analysis of the first preparation the lithium was weighed as sulfate after evaporation of the magnesium filtrate. In the analysis of the second preparation the lithium in one sample was determined as sulfate, and in the other as phosphate. By reason of the excessive time required for the determination of lithium as sulfate or phosphate, in the analysis of the other precipitates the lithium was precipitated as the aluminate and weighed in this form after the separation of the uranium and the divalent metal.

The following results were obtained in the analysis of these two preparations:

	Uranium %	Magnesium %	Lithium %
Found:			
Preparation 1	48.17	1.58	0.49
Preparation 2, sample a	48.12	1.63	0.52
Preparation 2, sample b	48.15	1.64	0.44
Calculated:			
$LiMg(UO_2)_3(C_2H_3O_2)_9.6H_2O$	48.23	1.64	0.47

It is obvious that analysis of the lithium salt precipitated by the magnesium uranyl acetate reagent gives results that correspond closely to the theoretical figures for the hexahydrated triple salt.

Lithium Cobalt Uranyl Acetate. A lithium acetate solution prepared by dissolving 0.506 gram of lithium carbonate in 6 ml. of glacial acetic acid gave 3.63 grams of triple salt on precipitation with the cobalt uranyl acetate reagent.

For analysis the uranium was separated by a double precipitation, and in the filtrate the cobalt was precipitated with α-nitroso-β-naphthol and weighed as Co_3O_4. After removal of the excess of the organic reagent from the cobalt filtrate the lithium was determined as $LiH(AlO_2)_2.5H_2O$ by a modification of the method suggested by Prociv (*10*).

The following results were obtained on the analysis of this preparation:

	Uranium %	Cobalt %	Lithium %
Found	46.73	3.67	0.51
Calculated:			
$LiCo(UO_2)_3(C_2H_3O_2)_9.6H_2O$	47.13	3.89	0.46
$LiCo(UO_2)_3(C_2H_3O_2)_9.7H_2O$	46.57	3.84	0.45

Here the agreement of the analysis with the theoretical figures for the hexahydrated triple salt is less satisfactory than for the lithium magnesium uranyl acetate. Indeed, the analytical results correspond better with the theoretical figures for a heptahydrated lithium cobalt uranyl acetate. However, the lack of agreement with the theoretical figures for the hexahydrate is no certain indication that the cobalt salt is a higher hydrate since the discrepancy may be explained in other ways, such as the presence of some hygroscopic water in the sample taken for analysis. The essential fact is clear enough—namely, that the salt precipitated from lithium solutions by cobalt uranyl acetate reagent is a triple salt.

Lithium Nickel Uranyl Acetate. A lithium acetate solution prepared by dissolving 0.499 gram of lithium carbonate in 6 ml. of glacial acetic acid gave 4.35 grams of triple salt on precipitation with the nickel uranyl acetate reagent. The yield in this precipitation is markedly higher than in the precipitations made with the other reagents under analogous conditions. This higher yield is probably an indication that the lithium nickel uranyl acetate is less soluble than any other of these lithium triple salts. The nickel salt is also distinguished from the other triple salts by its color, which is bright green, the colors of the other triple salts being various shades of yellow.

For analysis the uranium was separated by a double precipitation, and in the filtrate the nickel was determined with dimethylglyoxime. After removal of the excess of organic reagent from the nickel filtrate the lithium was determined.

The following results were obtained on analysis:

	Uranium %	Nickel %	Lithium %
Found:			
Sample a	46.13	3.91	0.45
Sample b	46.40	3.87	0.57
Calculated:			
$LiNi(UO_2)_3(C_2H_3O_2)_9.6H_2O$	47.14	3.87	0.46
$LiNi(UO_2)_3(C_2H_3O_2)_9.7H_2O$	46.58	3.83	0.45

The results for the uranium content of this nickel salt are even further from the theoretical figure for a hexahydrated triple salt and nearer the theoretical figure for a heptahydrated triple salt than the result obtained for the uranium content of lithium cobalt uranyl acetate. On the other hand, the results for the nickel content of the triple salt, very likely the most accurate of the three determinations, are definitely closer to the theoretical figure for the hexahydrate. This discrepancy, which is certainly real and not an apparent one arising from defects in the analytical method, cannot be ascribed to improper drying but probably to a slight decomposition of the salt by the method of washing required to separate the salt from the reagent. That a slight amount of selective leaching out of component salts of certain complex uranyl acetates may occur on washing with alcohol is demonstrated clearly by the examination of the salt precipitated from potassium solutions by these reagents. However, the above results show clearly enough that the salt precipitated from lithium solutions by the nickel uranyl acetate reagent is also a triple salt.

Lithium Iron Uranyl Acetate. A lithium acetate solution prepared by dissolving 0.450 gram of lithium carbonate in 7 ml. of glacial acetic acid gave 2.16 grams of triple salt on precipitation with the ferrous uranyl acetate reagent. To prevent oxidation of the reagent during precipitation an atmosphere of nitrogen was maintained above the reaction mixture. Because of the likelihood of change in composition by oxidation on oven-drying, the preparation was not dried at 100° to 105° C. as were all the other preparations of these triple salts, but was allowed to stand exposed to air at room temperature until the weight became constant. No change in the appearance of the crystals of the salt was observed after exposure to air for 24 hours.

For analysis the iron was separated first by precipitation with cupferron, the precipitate being ignited to ferric oxide for weighing. After removal of the excess of organic reagent the uranium and the lithium were separated and determined in the usual way.

The results of the analysis were as follows:

	Uranium %	Iron %	Lithium %
Found	45.53	3.38	0.35
Calculated:			
$LiFe(UO_2)_3(C_2H_3O_2)_9.6H_2O$	47.22	3.69	0.46
$LiFe(UO_2)_3(C_2H_3O_2)_9.9H_2O$	45.59	3.56	0.44

From this analysis it would appear that the air-dried preparation might be a hexahydrated triple salt containing a considerable proportion of hygroscopic moisture or that it might be a higher hydrate. The first possibility seems rather unlikely because the crystals taken for analysis appeared entirely dry. The second is more likely, especially in view of investigations that have been made on the composition of air-dried sodium triple acetates. Certain of these analogous salts have been found to exist as hydrates containing more than six molecules of water, the highest reported being nine molecules, which also appears to be the water content of this air-dried lithium iron uranyl acetate.

Lithium Manganese Uranyl Acetate. A lithium acetate solution prepared by dissolving 0.524 gram of lithium carbonate in 6 ml. of glacial acetic acid gave only a few minute crystals on

Table I. Comparative Sensitivity of Reagents toward Sodium

Type of Reagent	Reaction with a Given Quantity of Sodium: 10 mg.	5 mg.	2 mg.	1 mg.	0.5 mg.	0.2 mg.	0.1 mg.
Magnesium	+	+	+	+	+	+	+
Nickel	+	+	+	+	+	+	+
Cobalt	+	+	+	+	+	+	+
Zinc	+	+	+	+	+	+	−
Manganese	+	+	+	+	−	−	−
Copper	+	+	+	+	−	−	−
Cadmium	+	+	−	−	−	−	−
Mercury	−	−	−	−	−	−	−

precipitation with the manganese uranyl acetate reagent. In another preparation a lithium solution made by dissolving 1.016 grams of lithium carbonate in 10 ml. of glacial acetic acid gave only 0.341 gram of triple salt on precipitation with the reagent. Evidently the triple salt containing manganese is much more soluble than the other lithium triple salts here described.

For analysis the uranium was separated by a double precipitation, and in the filtrate the manganese was precipitated as the phosphate and weighed as the pyrophosphate. Because of the small size of the sample available for analysis no attempt was made to determine the lithium, though this element was qualitatively found to be a constituent of the salt.

The results of the analysis were as follows:

	Uranium %	Manganese %
Found	46.96	3.52
Calculated:		
$LiMn(UO_2)_3(C_2H_3O_2)_9.6H_2O$	47.25	3.63
$LiMn(UO_2)_3(C_2H_3O_2)_9.7H_2O$	46.69	3.59

The result for the manganese content is nearer to the theoretical figure for the heptahydrate than for the hexahydrate, and the result for the uranium content lies between the theoretical figures for the two hydrates. As with the other triple salts of this series, with the possible exception of the magnesium and zinc salts, there is also some uncertainty as to the degree of hydration of this salt, though there is no uncertainty that it is a triple acetate.

Nonprecipitation of Lithium by Certain Reagents. In similar experiments with the cadmium, mercury, and copper uranyl acetate reagents no precipitates were formed on mixing these reagents with the concentrated lithium acetate solutions, nor did any precipitates form even after vigorous stirring for considerable periods. It seems doubtful, therefore, whether the corresponding lithium triple salts exist, or, at least, whether they can be separated out by this method.

The cadmium and mercury uranyl acetate reagents are so insensitive toward sodium ion that they are of little practical value as analytical reagents, but the copper uranyl acetate reagent is a fairly sensitive reagent for sodium. This difference is illustrated by the results in Table I which were obtained by mixing 5 ml. of a given reagent with 1 ml. of sodium chloride solution and observing the presence or absence of a precipitate at the end of 30 minutes.

Though the copper uranyl acetate reagent is not nearly so sensitive toward sodium ion as the first four types of reagents listed in Table I, these other reagents are fairly sensitive toward lithium ion, as is shown by Table II. These results were obtained by mixing 5 ml. of a given reagent with 1 ml. of lithium chloride solution and observing the presence or absence of a precipitate at the end of 30 minutes. Though the particular kind of zinc uranyl acetate reagent used in these experiments is slightly less sensitive toward lithium than the magnesium, nickel, or cobalt uranyl acetate reagents, it is also proportionately less sensitive toward sodium. On the other hand, the manganese uranyl acetate reagent is more sensitive to lithium than the copper uranyl acetate reagent, though it has the same sensitivity toward sodium. The copper uranyl acetate reagent appears to be the only practical one that is free from this parallelism in sensitivity toward lithium and sodium, and for this reason it may be said to be more nearly specific for sodium than any other type of uranyl acetate sodium reagent. However, because it is only moderately sensitive toward sodium ion, it seems to be of more value as a qualitative reagent than as a quantitative reagent.

Composition of the Potassium Precipitates

All these reagents on being added to concentrated potassium acetate or chloride solutions yield copious crystalline precipitates, but irrespective of the particular reagent employed or of the experimental variations in the volume and concentration of the potassium solutions all such precipitates were found to have essentially the same composition. Only a single type of double salt, a potassium uranyl acetate in which the components are in a 1 to 1 ratio, is formed when these reagents for sodium are added to potassium solutions.

Table II. Comparative Sensitivity of Reagents toward Lithium

Type of Reagent	Reaction with a Given Quantity of Lithium: 20 mg.	10 mg.	5 mg.	4 mg.	3 mg.	2 mg.	1 mg.
Magnesium	+	+	+	+	+	+	−
Nickel	+	+	+	+	+	+	−
Cobalt	+	+	+	+	+	+	−
Zinc	+	+	+	+	−	−	−
Manganese	+	−	−	−	−	−	−
Copper	−	−	−	−	−	−	−
Cadmium	−	−	−	−	−	−	−
Mercury	−	−	−	−	−	−	−

Precipitation Experiments with Potassium Solutions

After precipitation of 5 ml. of saturated potassium chloride solution with the magnesium uranyl acetate reagent by the general procedure given above, 2.09 grams of air-dried salt were obtained. In a similar experiment with the nickel uranyl acetate reagent the yield was 2.31 grams. Precipitation of 10 ml. of potassium chloride solution containing 100 mg. of potassium per ml. by the addition of the potassium solution to the zinc uranyl acetate reagent produced 2.34 grams of the air-dried salt.

In the analysis of these preparations the uranium was precipitated as ammonium diuranate with carbonate-free ammonium hydroxide and weighed as U_3O_8. After evaporation of the filtrates from the uranium determinations the potassium was converted to sulfate and weighed in this form. Not more than traces of the divalent metals could be detected in any of these preparations. The water content was estimated by difference after calculating the metals to acetates. The results of the analyses are shown in Table III.

Table III. Composition of Precipitates Produced by Mixing Certain Reagents with Concentrated Potassium Chloride Solutions

Reagent	Sample	Uranium %	Potassium %	Water %
Magnesium uranyl acetate	a	48.53	7.56	1.89
	b	48.48	7.32	2.59
Nickel uranyl acetate	a	48.52	7.44	2.21
	b	48.67	7.52	1.77
Zinc uranyl acetate	a	48.55	7.55	1.79

Table IV. Theoretical Percentages of Uranium, Potassium, and Water Required for Potassium Uranyl Acetates

Formula of Salt	Uranium %	Potassium %	Water %
$KUO_2(C_2H_3O_2)_3.H_2O$	47.21	7.75	3.57
$KUO_2(C_2H_3O_2)_3.{}^1/_2H_2O$	48.06	7.89	1.82
$KUO_2(C_2H_3O_2)_3$	48.96	8.04	..

It is obvious that the same salt is precipitated by all three reagents. The agreement for the uranium and the potassium content of the three preparations is close, though the results for the water content do not agree very well. However, the lack of close agreement in the water content might be ascribed to the method of estimation. If the results in Table III are now compared with the theoretical figures given in Table IV for the uranium, potassium, and water content required by certain formulas for potassium uranyl acetates, it might reasonably be concluded that the precipitate produced in a potassium solution by a uranyl acetate sodium reagent is, in the air-dried state, a hemihydrated potassium uranyl acetate. On the other hand, further experiments demonstrated that the water in such an air-dried precipitate is largely or entirely in the form of hygroscopic moisture.

For example, another preparation produced by precipitating a potassium solution with zinc uranyl acetate reagent and drying the salt to constant weight in air was divided into two samples. The first sample on being dried to constant weight at 100° C. was found to lose 1.54 per cent of water. The second sample on being dried to constant weight at room temperature in a desiccator over phosphorus pentoxide lost 1.60 per cent of water. No change in the form of the crystals in either sample was produced by these methods of drying. That the second sample was free from water after drying was shown by a determination of the uranium and potassium content and a calculation of the total percentage of the components, uranyl acetate and potassium acetate, this being found slightly to exceed 100 per cent. The water content of this particular preparation as shown by these two determinations is below that required by formula for even the hemihydrate.

The water content of air-dried preparations was found to vary according to the humidity of the air at the time of drying, and samples dried over phosphorus pentoxide and then exposed to air differing in humidity absorbed different proportions of water. These experiments indicated that the potassium uranyl acetate precipitated from potassium solutions by sodium reagents is the anhydrous salt, and that this salt is slightly hygroscopic.

An unusual fact about all these preparations of potassium uranyl acetate is the noticeable discrepancy in the ratios of the two components, uranyl acetate and potassium acetate. These ratios as shown by analysis consistently differ from the theoretical 1 to 1 ratio. Thus if the uranyl acetate content of the five samples listed in Table III is taken as unity the proportions of potassium acetate in the same order are 0.95, 0.92, 0.93, 0.94, and 0.95. Though this discrepancy in the ratio might be taken as an indication of the admixture of a small proportion of another double salt in which the ratio of uranyl acetate to potassium acetate is 2 to 1 or higher, the actual reason seems to be that some of the potassium acetate is preferentially leached out of the salt by the alcohol used for washing, since the discrepancy in the ratio of the components is increased by excessive washing with alcohol. It can similarly be shown that the lithium and sodium triple acetates may also be noticeably decomposed by washing with alcohol. This decomposition of the complex uranyl acetates on being washed with alcohol is significant in explaining some of the differences that have been reported in the determinations of the composition of such salts. This is a source of error that must be considered in the application of such salts in quantitative measurements.

Summary

The salts precipitated from lithium solutions by uranyl acetate sodium reagents are always triple acetates analogous in composition to the triple acetates precipitated from sodium solutions by these reagents. Though the water content of most of the isolated lithium triple salts is slightly variable, depending upon the conditions of drying, approximately six molecules of water of hydration are present in the salts dried to constant weight at 100–105° C.

No precipitates were formed in concentrated lithium solutions by the experimental cadmium, mercury, and copper uranyl acetate reagents, and it is doubtful therefore whether the corresponding lithium triple salts exist. It seems certain that such lithium salts cannot be prepared by the method used in this investigation.

The same salt—$KUO_2(C_2H_3O_2)_3$—is precipitated from concentrated potassium solutions by all types of uranyl acetate reagents for sodium.

The copper uranyl acetate reagent prepared for use in these experiments appears to be a more nearly specific qualitative reagent for sodium than any other type of uranyl acetate sodium reagent, since it is a moderately sensitive reagent for sodium and yet forms no precipitate with lithium solutions.

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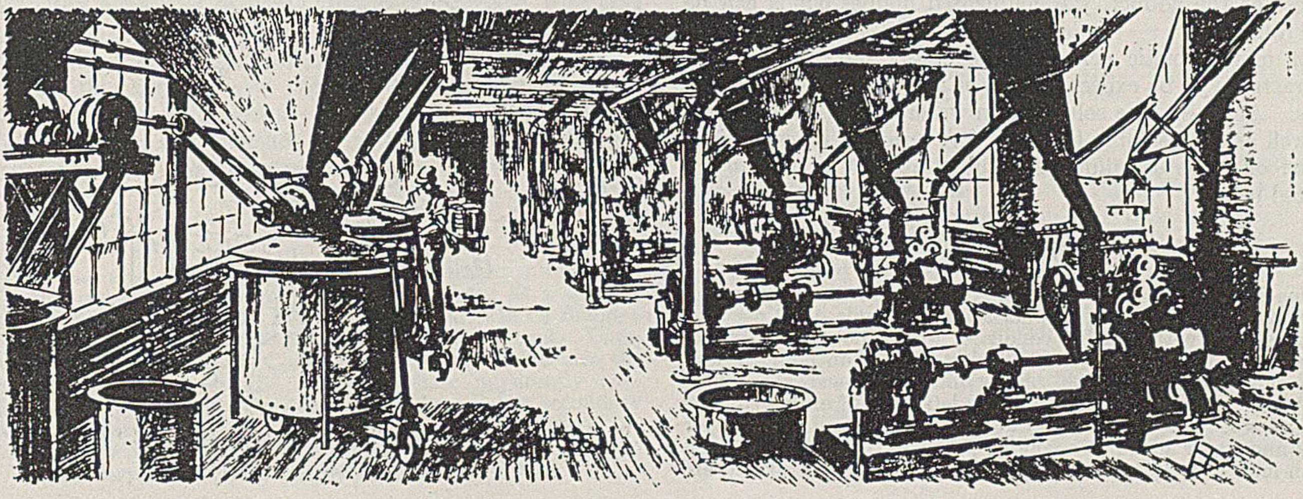

Analysis of Synthetic Resins Containing Maleic Acid

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FROM an analytical point of view the synthetic resins have not been sufficiently investigated (*1*, *11*). Most work has been done in connection with phthalic acid resins, which are simple alkyd resins, where the phthalic acid has been esterified by a polyhydric alcohol to high molecular compounds. Through saponification phthalic salts are obtained. By acidification the phthalic acid may be obtained in aqueous solution, whereas the oil acids and rosin acids precipitate. From this aqueous solution the lead salt may be precipitated and isolated for determination.

This principle forms the basis of the method of Fonrobert and Münchmeyer (*3*, *10*), and was employed by the author before he knew of these or other publications on the subject.

A more handy method is that of Kappelmeier (*4*), according to which 0.5 gram of resin dissolved in 5 ml. of benzene is saponified with about 25 ml. of approximately 0.5 *N* potassium hydroxide in c. p. ethyl alcohol. In this way potassium phthalate is precipitated with 1 molecule of alcohol. The precipitate is voluminous and needle-shaped. If commercial ethyl alcohol be used as solvent, only a small part can, according to the author's experience, be precipitated, whereas Kappelmeier claims to get sufficient for a technical analysis. After diluting with an equal volume of ethyl ether, the dilution is filtered through a glass filtering crucible, and washed with a mixture of ethyl ether and ethyl alcohol (1 to 1). Thorough washing is necessary, using 50 ml. in some six steps. Thereafter the precipitate is dried in a vacuum and weighed. The salt is very deliquescent.

Other methods have been published by Kavanagh (*6*) and Kerckow (*7*).

Although the maleic acid resins belong to the alkyd resins, the question here is more complicated, the maleic acid being combined with the abietic acid according to the diene synthesis. Publications concerning this matter have been compiled by Ellis (*2*). The configuration of the maleic-abietic acid is given in Figure 1. Before the process, the abietic acid had conjugated double bonds at *x* and *y*, while the maleic acid double bond was at *z*.

An analytical application of this process is the determination of the diene number according to Kaufmann (*5*) and Sandermann (*8*). By heating an oil or rosin with an excess of maleic anhydride in a suitable solution, and after treatment and separation of the excess maleic acid titrating this excess or the adduct, the conjugated double bonds can be determined.

Of maleic-abietic acid, a considerably more hydrophilic character is to be expected than of the other resinous products. At least some solubility in water should be expected, as well as an insoluble lead salt. A series of investigations based on these assumptions resulted in the procedure reported below.

Procedure

One-fifth gram of resin is dissolved in 5 ml. of benzene and saponified with 20 ml. of *N* potassium hydroxide in 90 per cent ethyl alcohol with a reflux condenser for an hour in a 100-ml. Erlenmeyer flask, followed by heating for half an hour without a condenser in a steam bath. Fifty milliliters of water are added to the residue, and the flask is again left for half an hour in the steam bath. The material is transferred to a 300-ml. Erlenmeyer flask and water added to a volume of 200 ml. Using methyl red as an indicator, approximately 6 to 7 ml. of 4 *N* acetic acid are added until the color approaches red. As the precipitated rosin is red in color, the dispersion will appear red, even though the liquid is orange. The precipitate therefore must settle before the color is observed; pH about 4.5. The material is filtered and washed twice, and as a smell of hydrogen sulfide often is noticed, boiled for 10 minutes. Next it is precipitated with 5 ml. of 1 to 10 lead acetate solution. The result is a flocculated colloidal precipitate, which, after cooling, is filtered through a Jena glass filtering crucible (10 G 4). Including the washings, the filtration will take about 2 hours, as the precipitate is sticky and the pores of the filter become clogged. The precipitate is dried for 45 minutes at 80° to 90° C. and weighed. The factor for the maleic acid–lead precipitate is approximately 0.30, assuming that 60 per cent of the maleic acid used in the resin is found by this procedure.

On heating the precipitate with dilute hydrochloric acid the maleic-abietic acid separates as a resinous lump, while phthalic and similar acids will dissolve.

The filtering crucible is best cleaned with alcoholic alkaline solution.

Precision

How carefully the various operations have to be performed will be obvious from the following.

If a double sample of resin is precipitated in half the solvent, the resulting precipitate is about one third of the above-mentioned. Roughly speaking, this applies to samples of both 10 and 20 per cent maleic acid. The conclusion must be that the maleic-abietic acid is divided between the water phase and the precipitated rosin. If the material contains only a small amount of maleic acid, and consequently but a small amount of maleic-abietic acid, the comparatively large quantity of rosin will absorb some maleic-abietic acid. If on the contrary much maleic-abietic acid and but little rosin are present, the rosin will absorb only a small quantity of maleic-abietic acid. The more free rosin present, the further must the aqueous solution be from saturation in order that the same percentage of maleic-abietic acid may be found present. If 0.1 gram is taken, practically the same percentage is found as with 0.2 gram. Consequently the lead precipitate is sufficiently insoluble not to demand special precautions, while the method has to be based upon the slight solubility of maleic-abietic acid.

If the sample is saponified for 15 minutes with 0.5 *N* potassium hydroxide solution, evaporated for 10 minutes in a steam bath, and transferred to cold water, the precipitate will be about one-

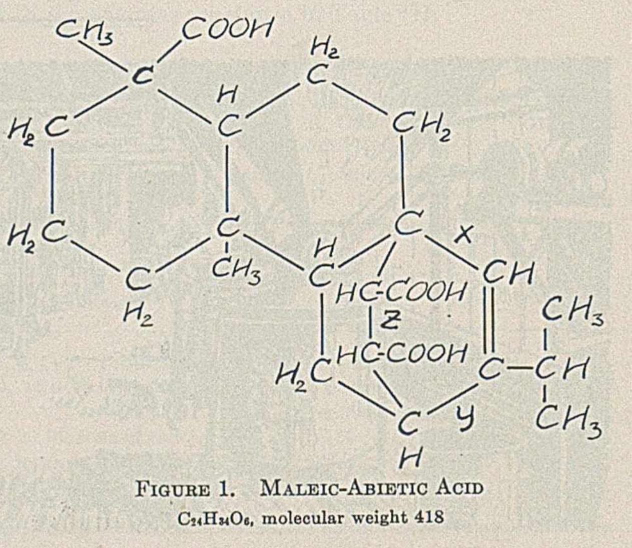

FIGURE 1. MALEIC-ABIETIC ACID

$C_{24}H_{34}O_6$, molecular weight 418

half that which is found when the above procedure is followed. If the resin is saponified for 4 hours and the aqueous solution is left for 4 hours in a steam bath, about five-sixths will be found. As the maleic-abietic acid to a great degree will be dehydrated, even if maleic acid is used as in the author's experiments, instead of maleic anhydride as in common manufacture, the object of the saponification is also hydration; consequently the treatment with alkali is continued in aqueous solution in the steam bath.

If acidification is effected through a 10-ml. excess of 4 N acetic acid, so that the resulting mixture is about 0.2 N as to acetic acid, the precipitate will be approximately one-fourth of the percentage according to the procedure. If only the rosin is precipitated at this acidity, while the acidity is adjusted to pH 5 before the lead precipitation, one-fourth is also found. This proves that the sensitive point is the rosin precipitation (*6*), while the lead precipitation is not influenced by this slight acidity.

In every case 1 ml. of 1 to 10 lead acetate solution will be stoichiometrically sufficient. If the double quantity is used, this will hardly be sufficient for a quantitative precipitation; 5 ml. are enough in every case and do not require accurate measuring.

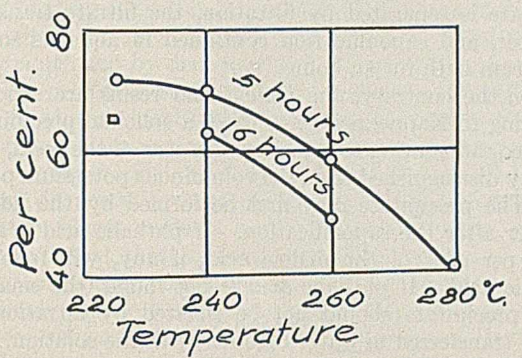

FIGURE 2. RELATION BETWEEN MALEIC ACID FOUND AND TEMPERATURE OF TREATMENT

When analyzing a synthetic varnish the precipitate from the acid precipitation may, on account of fatty acids, be too liquid for a filtration. In this case it may be shaken with 100 ml. of benzene, the benzene shaken with 50 ml. of water, and lead acetate added to the combined water fractions. The resulting precipitate will not be essentially below that of the above procedure. The benzene, however, will be dispersed in the aqueous solution, so that a distinct separation will be tedious.

The free maleic acid will not precipitate; 0.2 gram is the limit and 0.05 gram (maximum in 0.2 gram of resin) will certainly not precipitate from an aqueous solution, to which 4 N sodium hydroxide is added until the pH value is 4.5. With the quantities of potassium acetate present with this procedure, the dissociation of the lead acetate is decreased, so that the possibility of precipitation is even less.

With this knowledge of the method a reproducibility of 2 per cent may be attained. The other constituents of the resin, however, will influence the result, especially the products formed by a vigorous treatment.

Accuracy

The lead precipitate is heated with concentrated sulfuric acid (*9*) and transformed to lead sulfate. Computed as a tertiary salt, $(C_{24}H_{31}O_6)_2Pb_3$, on the average 84 per cent will be found—in exceptional cases below 80 per cent or over 90 per cent. Computed as a secondary salt, $C_{24}H_{32}O_6$ Pb, 108 per cent is also the average. Consequently the lead precipitate apparently consists of 33 per cent tertiary salt and 67 per cent secondary salt. The factors are:

Tertiary lead maleic-abietate:lead sulfate = 1.60
Secondary lead maleic-abietate:lead sulfate = 2.05

For computation of the precipitated lead salt as maleic acid, we have the factors:

Maleic acid:tertiary lead maleic-abietate = 0.160
Maleic acid:secondary lead maleic-abietate = 0.186

If the average composition of the precipitated lead salt is computed as above, we have the factor 0.177. Using this factor there is found on the average 60 per cent of the quantity of maleic acid used in the resins, the least in strongly processed products, the most in less processed ones.

In the curves of Figure 2 the percentage of maleic acid found is plotted against the highest temperature at which the resins were treated. In the upper curve the temperature was kept constant for 5 hours, in the lower one for 16 hours.

TABLE I. CONDITION OF MALEIC ACID DURING TREATMENT

Sample No.	Treatment Time	Treatment Temperature	Acid No.	Tertiary Lead Maleic-Abietate in Fraction 1	Total Maleic Acid Fraction 1	Total Maleic Acid Fraction 2	Total Maleic Acid Fraction 3	Sum of Three Fractions	Free Maleic Acid
	Min.	° *C.*		%	%	%	%		%
I	10	180	221	83	80.5	12.2	2.4	95.1	1.9
II	30	180	221	..	77.5	6.2	3.1	86.8	1.8
	Hours								
III	1	180	212	85	72.6	12.8	3.6	89.0	1.4
IV	5	225	200	85	72.4	7.9	4.2	84.5	0.5
V	14	260	36	83	57.4	9.9	3.3	70.6	0.05
VI	22	260	31	85	48.6	5.2	1.3	55.1	...

By the treatment the temperature was by steps brought up to this maximum. Some of the products are esterified, some not. The maleic acid content was between 10 and 18 per cent. The values are not influenced by these variations; on the contrary, a resin that contained 26.2 per cent of maleic acid, corresponding to 94.5 per cent of maleic-abietic acid, falls outside the curve and is plotted as a square. This was to be expected, as the total quantity of acid in a rosin is not present as indicated in Figure 1, and as maleic-abietic acid only can be formed when the conjugated system is present (*2*).

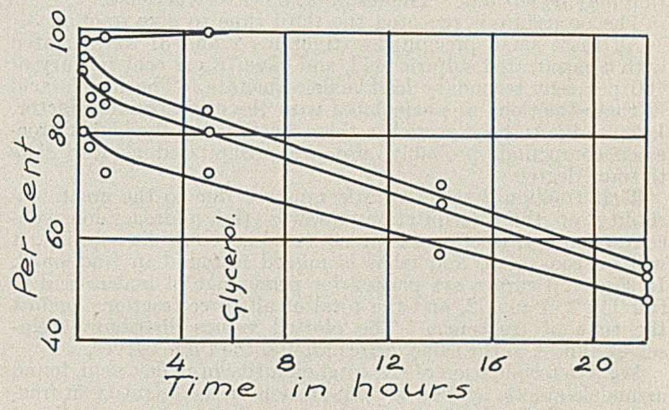

FIGURE 3. RELATION BETWEEN MALEIC ACID FOUND AND TIME OF TREATMENT

In order to account for the total quantity of maleic acid, the experiment represented in Table I and Figure 3 was conducted. Before the esterification this resin contained 15.1 per cent of maleic acid and after esterification 14.2 per cent, being prepared from 900 rosin, 160 maleic acid, and esterified with 210 glycerol containing 12 per cent of water. In the computation due regard is paid to the water content of the glycerol, the water formed during esterification, and half of the water which would disappear through complete dehydration of the maleic acid used. From the acid numbers it will be evident that about one half of the maleic acid is dehydrated. The theoretical acid number of the mixture is 284. If the maleic acid is dehydrated the figure will be 140. The author used an American rosin with an acid number of 161 and an iodine number of 137 (Hanus reagent, solution in carbon tetrachloride, 2 hours' standing). The acid number of maleic acid is computed as 968, its iodine number being 0.

The iodine numbers approach 90, a value corresponding to one double bond in maleic-abietic acid, and two in the remaining abietic acid. Before the esterification the maleic-abietic acid is computed at 54.8 per cent.

Other products, where the acid numbers have fallen comparatively more, show iodine numbers lower than those corresponding to a single double bond.

In Table I the second column indicates the time from the moment the total quantity of maleic acid is added to the rosin.

Where the temperature increases, the increase is made during the first hour.

Esterification with glycerol was made one hour after sample IV was taken out. According to theory, the acid number should fall to 0, as 10 per cent more glycerol was added than that corresponding to complete esterification.

A lead determination in the lead precipitates is computed as percentage of tertiary lead maleic-abietate, and the results are recorded in column 5. The corresponding average factor is used for computing the quantity of maleic acid indicated in column 6 as fraction 1. The computation is made as follows:

$$\frac{\text{Weight of lead precipitate} \times \text{average factor } (0.177) \times 10{,}000}{\text{Weight of sample} \times \text{percentage maleic acid used in resin}}$$

The maleic acid in the precipitates recorded as fractions 2 and 3 is computed against another factor as explained below.

The rosin acids isolated through filtration were again dissolved on the filter with the same quantity of alcoholic potassium hydroxide that was applied in the procedure proper, using more ethyl alcohol to wash the filter. This quantity of potassium hydroxide is not necessary for solution of the precipitate, but if the corresponding quantity of potassium acetate is not present at the precipitation of the acids, the rosin acids will not coagulate in a state fitted for filtration. Furthermore, the buffer action is necessary to regulate the hydrogen-ion concentration. The material is transferred to water and precipitated once more exactly as before. Only the cooking before the lead precipitation may be left out. The result is shown as fraction 2.

The procedure is repeated the third time to give fraction 3.

All these small precipitates (fractions 2 and 3) were treated with concentrated sulfuric acid, and gave 78 per cent tertiary or 100 per cent secondary lead maleic-abietate. The maleic acid in these fractions was calculated with the corresponding factor. Less lead is to be expected in these fractions, as the higher processed compounds probably also are precipitated as lead salts to some degree.

That fraction 2 seems erratic must be due to the great sensibility of the precipitation towards the hydrogen-ion concentration. If fraction 1 is precipitated in too acidic solution, it will be too small, and what is missed is found in fraction 2. In Figure 3 curves are plotted for percentage of maleic acid in fraction 1, 1 plus 2, and the total of all three fractions against the time of treatment. The plotted values distribute themselves almost to the same degree around the three curves.

For a determination of the total quantity of maleic acid, found as maleic-abietic acid by a computation of the quantity in fraction 1, we have the factors:

Sum of fractions : fraction 1 = 1.175
Maleic acid as maleic-abietic acid : fraction 1 = 0.208

The free maleic acid was arrived at by shaking 5 grams of resin dissolved in 50 ml. of benzene with 25 ml. of water. By way of control, 5 grams of rosin, also in 50 ml. of benzene, were shaken with 25 ml. of water in which 0.1 gram of maleic acid had been dissolved, and 50 ml. of benzene were shaken with 25 ml. of water in which 0.1 gram of maleic acid also had been dissolved. The shaking was done in a machine for a couple of hours, so that the maleic-abietic acid might find its equilibrium between the two phases. The 0.5 per cent found in sample IV corresponds to the quantity of maleic-abietic acid anticipated to be found in the water according to the above statements. Whether or not it corresponds to a blank is unimportant. The free maleic acid is hereafter below 2 per cent in sample I and decreases rapidly. It is determined through titration of the aqueous solution with 0.1 *N* sodium hydroxide, using phenolphthalein as an indicator.

In Figure 3 the free maleic acid is plotted downwards from the upper horizontal axis. In the interval between free maleic acid and maleic acid as maleic-abietic acid, combinations will be found, not reported here.

Immediately after beginning the experiment the author found 95 per cent of the maleic acid as maleic-abietic acid and 2 per cent as free maleic acid. No better result can be expected, considering that great quantities reacted further during the process, and that the addition of the maleic acid to the rosin required 2 hours.

Specificity

With this procedure colophony gives no lead precipitate; neither do the phenol-formaldehyde resins. The phthalic acid resins, however, form a crystalline precipitate, easily distinguished from that of maleic-abietic acid (*3*). The phthalic acid may be removed, when the saponification is made according to Kappelmeier (*4*); then the potassium phthalate is separated by filtration, the filtrate transferred to water, and saponification continued in aqueous solution in a steam bath for an hour.

If, on the contrary, the maleic acid resins are saponified according to Kappelmeier's method, a colloidal precipitate is obtained, amounting to some few per cent of the resin, which is easily distinguished from the voluminous potassium phthalate. The precipitate may first be formed by the addition of ether after the saponification. If phthalic acid is found, a few per cent of the maleic acid, if any, will follow the phthalic acid. If phthalic acid is not found, the small colloidal precipitate should not be isolated by filtration, but simply transferred to water together with the solution.

Summary

The literature contains no methods for the chemical analysis of maleic acid (anhydride) resins, but mentions the fact that such do not exist.

Considerations based on new theories regarding the constitution of these (the diene synthesis) have led to the method described above.

What has been utilized analytically is a chemical property: solubility in faintly acidic aqueous solution. This proves to be typical for maleic-abietic acid, as contrasted with the constituents of rosin and phenol-formaldehyde resins, while phthalic acid from phthalic resins may be removed in advance.

A quantitative determination of maleic-abietic acid is obtained. Its quantity is reduced during the production of resin from approximately 100 per cent to an average of about 60 to 70 per cent. The method may be employed as a control of the process, and to give an idea of how much maleic acid enters into an unknown resin, at least serving for its identification.

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Determination of Soybean Flour in Sausage by Nonfermentable Sugars

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ALTHOUGH much has been published in regard to the soybean's diversity of uses and the value of edible soybean flour as a low-cost source of protein, fat, calcium, phosphorus, and iron in the human diet (*9*, *23*), soybean flour has not yet attained appreciable retail distribution and, like any new food product, probably will not until after long and expensive consumer education. It is, however, reaching the public to a limited extent in certain manufactured food products, such as sausage and related meat products.

Federal regulations have long permitted the properly declared addition of cereal products up to 3.5 per cent in sausage. These materials are useful in binding the natural moisture content of the meat and in improving the texture and firmness of the product. The amount of cereal flour used can be readily controlled by determination of the kind and amount of starch present. Soybean flour is also a very effective binder in sausages and furthermore does not lower the protein content, since it contains twice as much protein as lean meat. However, the regulations of the Bureau of Animal Industry do not at present permit the use of soybean flour in meat products made in federal-inspected plants, on the sole ground that there is no quantitative method of determination and hence no method of check on the amount used. Accordingly its use is confined to intrastate business, where it is frequently restricted because of adoption of Bureau of Animal Industry regulations by local inspection authorities.

Qualitative Tests

These prohibitions can be readily enforced because effective qualitative tests for soybean flour are available. One depends on the liberation of ammonia from urea by the urease of the soybean (*16*, *18*). This sometimes fails because the urease has been inactivated by the "debittering" process (usually involving some form of steaming) applied to all edible soybean flours to make them acceptable to the American taste or by the cooking applied to certain types of sausage in manufacture. One method, which is based on obtaining a residue of hemicellulosic material by insolubility in alcoholic potassium hydroxide and microscopic identification in this residue of the typical spool-shaped subepidermal cells of the soybean, seems reliable (*16*, *25*). A serum precipitin test has also been described (*27*).

Bases for Quantitative Method

Soybean flour contains no starch; therefore some other basis for analysis must be sought. As the major and least variable constituents are protein and nonstarchy carbohydrates, one or both of these materials would seem to be the logical basis for a method of identification. The characteristic protein, glycinin, is specific for the soybean and, as it comprises about 50 per cent of the flour, seems an ideal basis for an analysis. However, this protein will be present in a large excess of meat proteins and its solubility properties vary with the amount of denaturization resulting from the various debittering processes and sausage preparation methods. Furthermore, a general method must also apply in the presence of a wide variety of possible accompanying materials, such as cereal proteins, liver, dried milk proteins, etc. An attempt by a commercial laboratory to develop a reliable chemical separation of the soybean protein, supported by the Soybean Processors Association and extending over about 3 years, has so far not been successful (*17*).

Recently a preliminary report has appeared on a promising method by which the soybean protein in sausage is determined biologically by means of a quantitative modification of the rabbit serum precipitin reaction (*14*). This method is now being further studied to determine its applicability to soybean flours of various preliminary histories (*13*).

A method which has been proposed for controlling the total amount of soybean flour and other carbohydrate-containing materials added, is based on the indirect determination of "nitrogen-free extract" which is essentially zero for meat but common to all carbohydrate-containing materials (*15*).

Reducing Sugar Method

Meanwhile the present author developed a direct carbohydrate method based on hydrolysis to reducing sugars and determination of the latter with Fehling's solution. It has been found possible to impart a considerable degree of specificity to this method by taking into account the particular nature of the carbohydrates of soybean flour and basing the determination on insoluble, nonfermentable sugars present, using a quick and convenient fermentation technique. This procedure eliminates interference from soluble sugars, starch, modified starch, and glycogen, which are the carbohydrate materials most apt to accompany soybean flour in meat products. Serious interference will be shown by materials high in pentosans, arabans, etc., such as whole-wheat flour, but such products are not normally added to sausages. The method appears to give results sufficiently accurate for control purposes. Although further experience will doubtless permit additional refinements, the author, not being directly concerned with analysis of meat products, is not in position to pursue the study further and therefore it seems advisable to present the method as so far developed.

Little work has been done to determine the particular carbohydrates present in soybeans or soybean flour. Fairly complete group analyses have been reported by Street and Bailey (*24*) and by Yukawa, who is quoted by Sato (*21*) as authority for the following analyses of the soybean:

	%		%		%
Total carbohydrates	21.69	Stachyose	3.52	Galactan	4.62
Sucrose	5.90	Araban	3.80	Crude fiber	3.82

After trying various procedures based on converting galactans to mucic acid, converting pentosans to furfural, utilizing the residue insoluble in alcoholic potassium hydroxide, and various methods of hydrolyzing the hemicelluloses to reducing sugars and distinguishing the soybean sugars from those derived from extraneously added dextrose, sucrose, starch, and lactose, by diastase, optical rotation, fermentation, etc., the procedure below was adopted. Although the procedure as given includes determinations of soluble and insoluble sugars, only the determination of nonfermentable sugars, is required to determine the presence of soybean flour. The other determinations are used only in case information is desired concerning added sugars and starches.

Method A. Insoluble Nonfermentable Sugars

1. PREPARATION OF SAMPLE. Take samples containing about 2 grams of soybean flour (50 grams of unknown sausage). Prepare samples as directed by the Association of Official Agricultural Chemists (*5*). (Grind, evaporate two or three times with 95 per cent alcohol, extract most of the oil with petroleum ether,

TABLE I. SOYBEAN FLOURS USED

Expt. No.	212	189	211.1	211.2	208.2
Type	Expeller (dehulled)	Expeller (whole beans)	Expeller	Aqueous (debittered)	Unknown
Moisture, %	4.10	6.35	3.80	6.00	6.50
Ash, %	5.62	5.31	5.62	3.31	5.80
Protein, %	52.15	45.86	48.67	67.15	46.38
Oil, %	5.88	6.09	8.63	4.40	3.94
Crude fiber, %	2.36	4.99	2.40	2.60	6.41
Nitrogen-free extract (by difference), %	29.89	31.40	30.88	16.54	31.15

TABLE II. GROUND MEAT AND DRIED AND DEOILED MEAT POWDERS USED

Expt. No.	193.1[a]	193.2	194.2	207
Description	Ground lean pork and beef	193.1 dried and deoiled	Like 193.2	Like 193.2
Moisture, %	73.34	26.29	4.83	2.01
Ash, %	0.93	...	...	...
Protein, %	22.50	...	67.85	84.44
Oil, %	4.00	1.11	1.60	7.86
Crude fiber, %	None	...	...	...
Nitrogen extract, (by difference), %	−0.23	...	...	...

[a] 217 and 218 like 193.1.

and regrind.) Filter the petroleum ether extract through the same filter paper as used under (2).

2. REMOVAL OF WATER-SOLUBLE SUGARS. Place the weighed samples in iodine number flasks and wash by decantation with neutralized 50 per cent alcohol, pouring the liquid through an 11-cm. No. 42 Whatman filter paper coated with 0.3 cm. (0.125 inch) of washed Filter-Cel. Transfer most of the solid to the paper and wash five times more with the 50 per cent alcohol. Total washings should amount to about 200 cc.

3. DETERMINATION OF SOLUBLE SUGARS (OPTIONAL). The amounts of added sugars may be determined by treating the filtrate as directed (*2*) starting with "evaporate on a steam bath to 20 to 30 cc.", and (*3*), but using the inversion conditions of (*4*) instead of (*3*). Reducing sugars obtained from commercial soybean flours before inversion are usually negative or so small as to be negligible, while sugars after inversion range from 2.12 per cent (one sample) to 12 to 14 per cent invert sugar (11.5 to 13.5 per cent as dextrose).

4. DETERMINATION OF INSOLUBLE SUGARS. Transfer the washed residue and Filter-Cel, after drying a short time to expel most of the alcohol, to the original iodine number flask, and add 120 cc. of 2.5 per cent hydrochloric acid from a small wash bottle, washing the paper and sides of the flask. [Sulfuric acid hydrolysis followed by barium hydroxide neutralization assists clarification and reduces the salt content of the solutions but hydrolysis is somewhat less complete. Hydrochloric acid was also found more effective on rice bran hemicelluloses by Fukagawa and Ri (*12*) and by Yanovsky (*26*).]

Provide the flask with rubber-stoppered reflux air condensers and hold in a boiling saturated salt bath for 3 hours. Nearly neutralize with 10 per cent sodium hydroxide (alkaline to methyl orange and acid to litmus), transfer to a 250-cc. volumetric flask, make nearly to volume with hot water, add 2 cc. of 50 per cent phosphotungstic acid, shake, and allow to cool to room temperature. Make to volume, shake, and centrifuge or filter. Pipet 200 cc. of centrifugate to a 250-cc. volumetric flask, add 30 cc. of 50 per cent phosphotungstic acid solution, make to volume with water, shake thoroughly, and centrifuge. Test for complete precipitation with a crystal of phosphotungstic acid. Pipet 200 cc. into a 250-cc. volumetric flask, and add dry potassium chloride in slight excess to precipitate excess phosphotungstic acid. (If no precipitate forms add 1 to 2 cc. of phosphotungstic acid solution.) Add 1 drop of methyl orange solution and neutralize to methyl orange and litmus. Cool, make to volume, shake, and filter through dry No. 42 Whatman paper. If desired, determine per cent of insoluble sugars by the A. O. A. C. method (*7*) on an aliquot. (For soybean flour this figure will be about 11 to 12 per cent of invert sugar or 10.5 to 11.5 per cent of dextrose.) [See (*6*) in connection with the preparation of the solution for sugar analysis. If total insoluble sugars are determined at this point, the amount of starch present may be calculated approximately from the difference between total insoluble sugars and nonfermentable insoluble sugars. Soybean flour shows about 2 per cent (invert sugar), insoluble fermentable sugars.]

5. DETERMINATION OF NONFERMENTABLE SUGARS. [This quick fermentation method is adapted from Bailey (*8*), who used it to determine lactose in frankforts, from Somogyi (*22*), and others. According to Somogyi, less than 10 minutes is necessary to remove dextrose completely while over 30 minutes causes removal of maltose, etc. Fermentation time does not seem very important with soybean flour, but the 45-minute period appears to give slightly better results than shorter times. The method seems to rest on adsorption rather than fermentation (*20*). Toluene may be added to preserve the solutions, if desired, without hindering the removal of "fermentable" sugars. The older method of 3- to 5-day fermentation (*1*) caused practically complete destruction of the sugars.]

Preparation of yeast. Wash fresh bakers' yeast five times by stirring up with three times its volume of distilled water and centrifuging. The last washing should be clear. Keep 25 per cent suspension in water at about 0° C. Prepare fresh at least once a week.

Fermentation. Place 10 cc. of the yeast suspension in a 100-cc. centrifuge tube, centrifuge, pour off water, and dry inside of tube with filter paper. Add about 60 cc. of the sugar solution from (4) through a funnel (first diluting, if necessary, to contain not over 0.1 per cent concentration of fermentable sugars). Stir up the yeast well and let stand 45 minutes, preferably at 30° C. Stir up once more during this period. Centrifuge and filter through a dry No. 42 Whatman paper. Analyze for per cent of invert sugars by the A. O. A. C. method (*7*). Control tests on the yeast activity should be run on 0.1 per cent dextrose solutions. The dextrose should be completely removed.

6. CALCULATION OF RESULTS.

$$\% \text{ nonfermentable sugars in sample} \times 9.4 = \% \text{ soybean flour in sample}$$

TABLE III. ANALYSES OF SOYBEAN FLOURS BY METHOD A

Expt. No.	212.1	205.1	208.1	208.2	211.1	216.2	216.4
No. of flour	212	189	208.1	208.2	211.1	211.2	
Type	Expeller	Expeller	Expeller	Solvent	Expeller	Aqueous process	Mohican brand cornstarch
Soluble sugars as % invert sugars	11.80 11.88	11.65 11.65	13.83 13.77	14.25 13.83	14.94 13.97	2.12 2.12	... ...
Insoluble sugars as % invert sugars	11.48[a] 11.52[a]	12.50[a] 12.75[a]	11.43[a] 11.51[a]	12.63[a] 12.63[a]	13.32[a] 12.42[a]	12.42 12.42	98.91 98.91
Insoluble sugars as % invert sugars after fermentation	9.34 9.34	10.05 10.15	9.27 9.22	9.87 9.87	10.04 9.69	10.31 10.31	0.34 0.00

[a] Filter paper included in HCl hydrolysis. This was found to increase the % sugars by about 10 mg. of dextrose (0.5% in most of above cases) and hence was discontinued. The figure for sugars after fermentation is not affected.

TABLE IV. METHOD A ON GROUND MEAT AND MEAT POWDERS

Expt. No.	205.2	210.3	217.1	218.1
No. of sample	193.2	207	217[a]	218[a]
Description	Powder	Powder	Ground meat	Ground meat
Soluble sugars as % invert sugars	0.00[b] 0.00[b]	0.35 0.17	0.045 0.062	0.198 0.204
Insoluble sugars as % invert sugars	1.31[c] 1.31[c]	1.40 1.41	0.046 0.075	0.055 0.043
Insoluble sugars as % invert sugars after fermentation	0.00 0.00	0.052 0.102	0.009 0.018	0.0036 0.0075

[a] Like No. 193.1. [b] Not hydrolyzed. [c] Filter paper included.

TABLE V. METHOD A ON KNOWN MIXTURES WITH SOYBEAN FLOUR

Expt. No.	214.1	217.2	214.3	214.5a	214.5b
Composition, %:					
Soybean flour	4.0	4.762, No. 212	4.0, No. 208.2	3.0	5.82
Ground meat	96.0	95.238	96.0	96.0	92.25
Modified starch	....	....	....	0.9	1.74
Dextrose	....	....	....	0.1	0.19
Found:					
Soluble invert sugars, %	0.53 0.58	0.64 0.48	0.66 0.57	0.51	0.97
Insoluble invert sugars, %	0.49 0.51	0.733 0.817	0.59 0.57	1.21	2.26
Insoluble sugars after fermentation (D), %	0.400 0.389	0.508 0.532	0.43 0.40	0.32	0.63
Calcd. soybean flour ($10 \times D$), %	3.95	5.2	4.15	3.2	6.3
Error, %	−0.05	+0.44	+0.15	+0.2	+0.48
Corrected soybean flour ($9.4 \times D$), %	3.72	4.9	3.9	3.0	5.9

Table VI. Method B, Direct Hydrolysis

Expt. No.	212.3	213.1	217.3	214.2	214.4	210.2
Sample	Flour 212	Meat powder 207	Ground meat 217	4% flour 212, 96% ground meat	4% flour 208.2, 96% meat	15.0% soybean flour 4.5% modified starch 0.5% dextrose 80.0% meat powder 207
Total sugars as invert sugars, %	23.63 23.56	1.89 1.99	0.525 0.506	1.21 1.30	1.32 1.26	10.82 10.48
Nonfermentable sugars as invert sugar, (*C*) %	14.30 14.45	0.55 0.42	0.208 0.208	0.65 0.68	0.68 0.66	2.38 2.35
Calculated soybean flour (*C*/0.144), %	...	..	...	4.6	4.7	16.4
Error, %	...	..	...	+0.6	+0.7	1.4[a]
Corrected soybean flour (*C* − 0.10)/1.44, %	...	..	...	3.92	3.95	15.7

[a] Converted to 22.5% protein basis $\left(1.4 \times \frac{84.0}{22.5}\right)$ this error would be +0.37%.

Experimental Results

Table I gives data on the representative commercial soybean flours used. These are all low-fat flours such as are used in meat products, and in manufacture all have passed through a deoiling and a debittering process. Sample 211.2 was debittered with dilute sulfur dioxide solution which markedly altered its composition. Surprisingly enough, even this flour falls fairly well in line by the analytical method described.

Table II gives similar data on the meat samples used in making up the knowns. All samples consisted of equal parts of lean beef and pork muscle.

Table III gives data obtained on the soybean flours by Method A. The figures for soluble sugars and insoluble sugars are included as a matter of interest although they do not enter into the calculation of soybean flour. They may be used if it is desired to determine added starches and sugars simultaneously with the soybean flour. The unusual composition of sample 211.2 has been commented on above. Sample 216.4 shows the virtually complete absence of interfering materials in commercial edible cornstarch. Table IV shows that only very small amounts of interfering substances are obtained from the meat itself.

Table V shows that results for known mixtures accurate enough for control work are obtained by using the representative factor of 10.0 per cent for soybean flours. With the one exception shown, these and other determined values are somewhat high, showing that allowance should be made for the small blank correction for the meat and for the volumes occupied by the precipitates in the aliquot procedure used. Not enough data are yet available to determine the extent of these corrections with much confidence, but it can be seen that the corrected factor 9.4 gives close agreement with the correct values.

Short Method

The two reasons for washing the sample with 50 per cent alcohol are to remove unfermentable lactose if present and to remove most of the nonfermentable reducing substances derived from the meat itself. Lactose could be tested (*16*) for and determined (*8*) separately if present and a correction for this and for a blank meat determination applied to total nonfermentable sugars. This would provide no simplification, however. If lactose is absent a considerably shorter procedure omitting the washing step can be used, as shown under Method B which is advanced only tentatively at present, since not enough data are available to determine the general validity of the blank correction.

Method B. Total Nonfermentable Sugars

Weigh 50-gram ground samples of sausage into iodine number flasks and hydrolyze as under A-4. After hydrolysis and neutralization, extract most of the fat from the solution by shaking up with petroleum ether three times and removing the latter with a pipet. Wash the petroleum ether extract once with a small amount of water and add the water to the hydrolyzate. Heat briefly to expel traces of solvent and proceed as under A-4 and A-5.

$$\frac{\%\text{ nonfermentable sugars}}{0.144} = \%\text{ soybean flour (uncorrected)}$$

Representative data determined by this method are given in Table VI. The uncorrected errors are somewhat higher; hence Method A is favored at present. The chief cause of the higher results by Method B lies in the nonfermentable reducing substances derived from the meat itself. These are probably not all true sugars (*11*). Further experience with the method should enable a satisfactory correction factor based on the protein content of the sample to be worked out. Apparently this will be smaller than the factor obtained by blank determinations on meat. This may be due to promotion of the fermentative removal of these materials by the presence of an excess of fermentable sugars (*10*, *19*). Trial application of the correction factor of 0.1 per cent invert sugars is shown in the last line of Table VI.

Acknowledgment

Valuable assistance was given by other members of the laboratory staff, especially Jean Constable who made all the sugar determinations.

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Quantitative Determination of Aromatic Hydrocarbons by New Method

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A simple method has been developed for the rapid quantitative determination of aromatics in hydrocarbon mixtures boiling in the gasoline and naphtha range.

The method is a purely physical one and is based on the measurement of the specific dispersion of the sample. The dispersion is measured on an ordinary Abbé or, where more accurate results are desired, on a Pulfrich refractometer.

The theory underlying the method has been checked on a number of synthetic mixtures.

SIMPLE and accurate methods for the determination of aromatics in hydrocarbon mixtures have always been desirable, but they become particularly so in view of the rapid development of hydrocarbon chemistry in the last few years.

The method described here is a purely physical one that consists essentially in determining the specific dispersion of the hydrocarbon mixtures. In contrast to the chemical or physicochemical methods, it is not necessary to remove the aromatics from the mixture. As herein described, the method is limited to aromatic hydrocarbons boiling below naphthalene (219° C.) and covers the boiling ranges of gasolines and naphthas. In principle the method of specific dispersion analysis may be applied to nonhydrocarbon material.

A critical discussion of the advantages and disadvantages of other methods suggested for the determination of aromatics and a comparison with the present one will be reserved for a subsequent publication.

Principle of the Method

As is well known, the dispersion, Δ, of a substance is the numerical difference in the indices of refraction for two specified wave lengths. The specific dispersion, δ, is the dispersion, Δ, divided by the density, d, both taken at the same temperature. For practical purposes, it is convenient to use the H_α (6563 Å.) and H_β(4861 Å.) lines and multiply by the factor 10,000. The specific dispersion, δ, at the temperature, *t*, is thus defined by means of the expression

$$\delta^t = \frac{n^t{}_{H_\beta} - n^t{}_{H_\alpha}}{\mathrm{d}^t{}_4} \times 10^4$$

As a standard temperature, in line with other physical-chemical constants, the temperature 20° C. has been chosen. In the authors' tables the dispersion, $\Delta_{H_\beta - H_\alpha}$, is also multiplied by the factor 10^4.

The authors' method of analysis is based on the fundamental fact, established particularly by Darmois (*1*) in 1920 and further developed by Waterman and Perquin (*12*), Ward and Fulweiler (*10*), Fuchs and Anderson (*3*), and Ward and Kurtz (*11*), that all saturated hydrocarbons, paraffins, or naphthenes, either mono- or polycyclic, independent of their molecular weights, have a practically constant specific

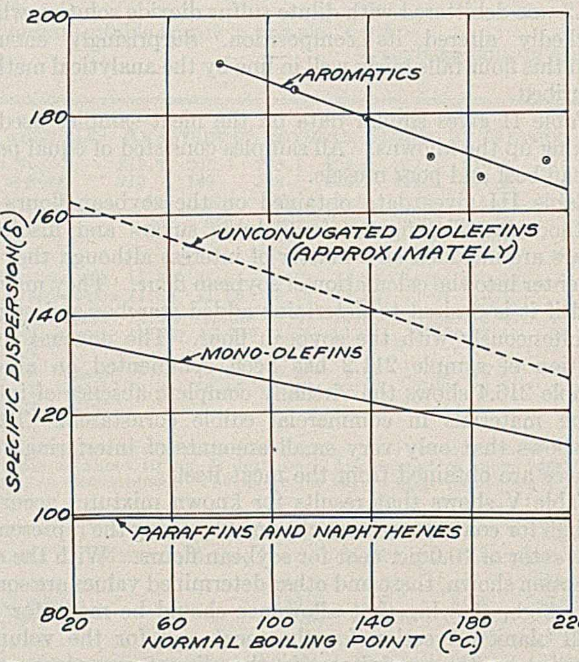

FIGURE 1. SPECIFIC DISPERSION *vs.* BOILING POINT FOR VARIOUS HYDROCARBON CLASSES

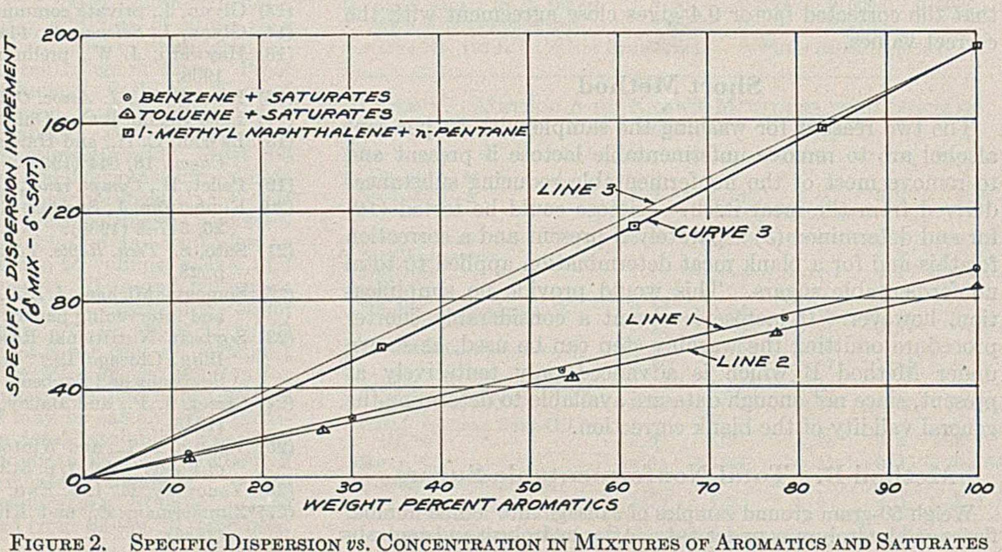

FIGURE 2. SPECIFIC DISPERSION *vs.* CONCENTRATION IN MIXTURES OF AROMATICS AND SATURATES

TABLE I. UNPUBLISHED DATA ON DISPERSION AND SPECIFIC DISPERSION OF HYDROCARBONS[a]

	Temp. °C.	d^t_4	n^t_D	$n^t_{H_\beta}$	$n^t_{H_\alpha}$	$\Delta^t_{\beta-\alpha}$	$\delta^t_{\beta-\alpha}$	Reference
Paraffins								
n-Pentane	20	0.62624	....	1.36200	1.35587	61.3	97.9	*13*
2-Methylbutane	20	0.61972	....	1.35827	1.35218	60.9	98.3	*13*
n-Hexane	20	0.65943	....	1.37950	1.37300	65.0	98.6	*13*
2-Methylpentane	20	0.65316	....	1.37609	1.36961	64.8	99.2	*13*
3-Methylpentane	20	0.66435	....	1.38114	1.37470	64.4	96.9	*13*
2,2-Dimethylbutane	20	0.64919	....	1.37344	1.36695	64.9	99.9	*13*
2,3-Dimethylbutane	20	0.66166	....	1.37965	1.37313	65.2	98.5	*13*
n-Heptane	20	0.68378	....	1.39247	1.38573	67.4	98.6	*13*
	20	0.6836	1.3870	1.39173	1.38502	67.1	98.1	G. W.
	80	0.6323	1.3593	1.36358	1.35752	60.6	95.9	G. W.
2-Methylhexane	20	0.67869	....	1.38967	1.38292	67.5	99.5	*13*
2,2-Dimethylpentane	20	0.67388	....	1.38703	1.38025	67.8	100.6	*13*
2,3-Dimethylpentane	20	0.69514	....	1.39680	1.39007	67.3	96.8	*13*
2,4-Dimethylpentane	20	0.67275	....	1.38620	1.37956	66.4	98.7	*13*
3,3-Dimethylpentane	20	0.69330	....	1.39575	1.38901	67.4	97.2	*13*
2,2,3-Trimethylbutane	20	0.69007	....	1.39430	1.38751	67.9	98.4	*13*
n-Octane	20	0.70280	....	1.40252	1.39562	69.0	98.2	*13*
3-Methylheptane	20	0.70584	....	1.40344	1.39656	68.8	97.5	*13*
2,3-Dimethylhexane	20	0.71234	....	1.40617	1.39922	69.5	97.6	*13*
2,5-Dimethylhexane	20	0.69426	....	1.39772	1.39081	69.1	99.5	*13*
3,4-Dimethylhexane	20	0.71951	....	1.40924	1.40224	70.0	97.3	*13*
3-Methyl-3-ethylpentane	20	0.72742	....	1.41280	1.40581	69.9	96.1	*13*
2,2,3-Trimethylpentane	20	0.71613	....	1.40790	1.40094	69.6	97.2	*13*
2,2,4-Trimethylpentane	20	0.69196	....	1.39640	1.38944	69.6	100.6	*13*
	20	0.6918	1.3912	1.39621	1.38924	69.7	100.7	G. W.
	80	0.6404	1.3633	1.36764	1.36131	63.3	98.8	G. W.
n-Nonane	20	0.71808	....	1.41058	1.40353	70.5	98.2	*13*
n-Hexadecane	20	0.77387	....	1.44002	1.43242	76.0	98.2	*13*
Unsaturates (Straight Chain)								
2-Ethylhexene-1	20	0.7268	1.4210	1.42426	1.41544	88.2	121.4	G. W.
Diisobutene	20	0.7370	1.4122	1.4184	1.4098	86.0	116.9	G. W.
Naphthenes								
Ethylcyclobutane	20	0.72787	....	1.40719	1.40001	71.8	98.6	*13*
Cyclopentane	20	0.74542	....	1.41145	1.40442	70.3	94.3	*13*
Methylcyclopentane	20	0.74869	....	1.41488	1.40764	72.4	96.7	*13*
	20	0.749	1.4100	1.4153	1.4080	72.7	97.1	G. W.
Cyclohexane	20	0.77867	....	1.43157	1.42405	75.2	96.6	*13*
	20	0.7786	1.4254	1.43053	1.42307	74.6	95.9	G. W.
	80	0.7201	1.3953	1.40022	1.39345	67.7	93.9	G. W.
Methylcyclohexane	20	0.76944	....	1.42838	1.42085	75.3	97.9	*13*
	20	0.7700	1.4223	1.42754	1.42003	75.1	97.5	G. W.
	80	0.7170	1.3946	1.39961	1.39278	68.3	95.2	G. W.
Ethylcyclopentane[b]	20	0.7632	1.4203	1.4252	1.4179	73.0	95.6	G. W.
Isopropylcyclopentane	20	0.7764	1.4263	1.4315	1.4241	74.4	95.8	G. W.
Isopropylcyclohexane	20	0.80232	....	1.44641	1.43867	77.4	96.5	*13*
n-Butylcyclopentane	20	0.7832	1.4321	1.4375	1.4300	75.4	96.3	G. W.
Isobutylcyclopentane	20	0.7806	1.4301	1.4353	1.4278	75.5	96.7	G. W.
tert-Butylcyclopentane	20	0.7911	1.4341	1.4396	1.4320	76.4	96.6	G. W.
sec-Butylcyclopentane	20	0.7941	1.4361	1.4415	1.4339	75.7	95.4	G. W.
tert-Amylcyclopentane	20	0.8071	1.4457	1.4511	1.4433	78.0	96.6	G. W.
3-Cyclopentylpentane	20	0.8099	1.4443	1.4498	1.4422	76.7	94.7	G. W.
Neopentylcyclohexane	20	0.7989	1.4417	1.4473	1.4394	79.0	98.9	G. W.
Cyclohexylcyclopentane	20	0.8774	1.4726	1.4784	1.4700	83.7	95.4	G. W.
1,3-Dicyclohexylbutane	20	0.8793	1.4800	1.4860	1.4775	85.4	97.2	G. W.
Unsaturated Cyclics								
Cyclohexene	20	0.8092	1.4452	1.4520	1.4425	94.7	117.1	G. W.
Methylcyclopentene[b]	20	0.7791	1.4322	1.4389	1.4294	95.1	122.0	G. W.
Ethylcyclopentene	20	0.8053	1.4440	1.4507	1.4412	95.4	118.7	G. W.
n-Propylcyclopentene	20	0.8062	1.4461	1.4528	1.4434	94.3	117.0	G. W.
n-Butylcyclopentene	20	0.8138	1.4496	1.4562	1.4468	93.7	115.2	G. W.
tert-Butylcyclopentene	20	0.8021	1.4421	1.4486	1.4397	88.8	110.7	G. W.
tert-Amylcyclopentene	20	0.8256	1.4554	1.4618	1.4527	90.8	110.0	G. W.
4-*tert*-Butylcyclohexene	20	0.8315	1.4602	1.4667	1.4575	91.6	110.2	G. W.
4-*tert*-Amylcyclohexene	20	0.841	1.4676	1.4740	1.4649	91.3	108.5	G. W.
Aromatics								
Benzene	20	0.8789	1.5011	1.51318	1.49646	167.2	190.2	G. W.
	80	0.8135	1.4640	1.47505	1.45982	152.3	187.2	G. W.
Toluene	20	0.8669	1.4964	1.50781	1.49178	160.3	184.9	G. W.
	80	0.8097	1.4647	1.47539	1.46062	147.7	182.4	G. W.
Ethylbenzene	20	0.8681	1.4957	1.50668	1.49151	151.7	174.7	G. W.
o-Xylene	20	0.8796	1.5046	1.51594	1.50013	158.1	179.7	G. W.
m-Xylene	20	0.8647	1.4973	1.50869	1.49301	156.8	181.3	G. W.
p-Xylene	20	0.8616	1.4957	1.50709	1.49141	156.8	181.9	G. W.

[a] For lack of a definite value for the temperature coefficient some of the authors' own values (G. W.) are reported to the fourth decimal place only.

[b] The cyclopentanes and -pentenes used were synthesized by H. Pines of the Universal Oil laboratories, and the authors gratefully acknowledge the loan of these hydrocarbons.

dispersion of 99 ± 1. The specific dispersions of aromatics and olefins are substantially higher, as illustrated in Figure 1, which is based on data compiled by Fuchs and Anderson (*3*), Ward and Kurtz (*11*), and the authors' own determinations. The latter are given in Table I, together with recent measurements of Wibaut, Smittenberg, and co-workers (*13*).

In first approximation, the specific dispersion increments due to aromatics or olefins are straight-line functions of their concentration. For aromatics this is shown in Figure 2. Line 1 shows the specific dispersion of benzene in mixtures with *n*-heptane and cyclohexane and line 2 shows toluene in mixtures with 2,2,4-trimethylpentane and methylcyclohexane. The experimental points are drawn in and indicate the deviation. Measurements on these two series were made with a Pulfrich refractometer. Whereas these two mixtures represent close-boiling mixtures, which can be expected to be typical of mixtures obtained in practical fractionations, curve 3 represents an extreme case of liquids with widely differing boiling ranges and densities—namely, 1-methylnaphthalene (boiling point 243° C., $d_4^{20} = 1.0201$) and *n*-pentane (boiling point 36.08° C., $d_4^{20} = 0.6261$)—based on data given in Table II. Even in this case the deviation from linearity is not large.

TABLE II. MIXTURES OF *n*-PENTANE AND 1-METHYLNAPHTHALENE

	No. 74	No. 74-A	No. 74-B	No. 74-C	No. 74-D
Weight %					
1-Methylnaphthalene	0	33.40	61.57	82.80	100
n-Pentane	100	66.60	38.43	17.20	0
d_4^{20}	0.6259	0.7270	0.8338	0.9308	1.0201
n_D^{20}	1.3576	1.4222	1.4920	1.5564	1.6170
Z	41.8	38.4	34.4	30.0	24.3
Δ (Abbé)	64.7	118.0	181.2	243.1	303.1
δ (Abbé)	103.4	162	217	261	297

For olefins the effect of concentration on specific dispersion is shown in Figure 3; here the specific dispersion of a mixture of 2-ethylhexene-1 with saturated hydrocarbons is plotted against the experimental bromine number.

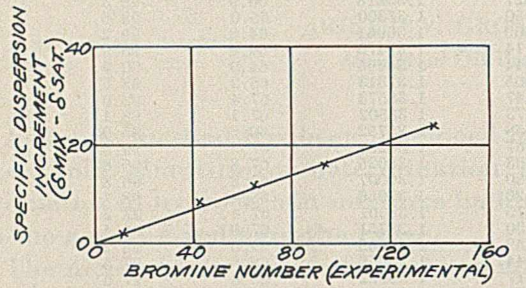

Figure 3. Effect of Olefin (2-Ethylhexene-1, Bromine No. 138) in Raising Specific Dispersion of Saturates

It is a very important fact that this relationship between increase in specific dispersion and the concentration of the double bond is general and holds good within reasonable accuracy, regardless of whether this concentration is changed by mixing an olefin with saturated hydrocarbons or whether the change is produced in the molecule of the olefin itself by changing the number of carbon atoms. It is true, therefore, also for diolefins, as well as for cyclic mono- and diolefins. This is illustrated in Figure 4, based on data of Tables I and XI.

The only exceptions are the conjugated diolefins. Conjugation produces abnormally high specific dispersions. Mixtures likely to contain them must be tested, and if present, they have to be eliminated by means of the Diels-Alder reaction as described below.

Any accurate method for determining unsaturation, such as bromine, iodine, or hydrogen number, etc., permits one to calculate the specific dispersion increment contributed by the double bonds. (Any inherent error in the determination of unsaturation will, of course, enter also into the method and should be guarded against. It is recommended that the bromine number, as well as the dispersion, of a known aromatic-free sample always be determined as a check.)

When bromine numbers are used to determine the unsaturation the following formula may be used:

$$\delta_{\text{olefins}} - \delta_{\text{saturates}} = \Delta\,\delta_{\text{olefins}} = 0.16 \times \text{bromine number}$$

For example, in a hydrocarbon mixture of bromine number 10, the increment due to olefins will be 1.6 specific dispersion units.

The specific dispersion of a mixture of paraffinic, naphthenic, aromatic, and olefinic hydrocarbons boiling in the gasoline range can be expressed within reasonable accuracy by the equation

$$\delta_{\text{mixt.}} = \delta_{\text{sats.}} + (\delta_{\text{arom.}} - \delta_{\text{sats.}}) \times \frac{\text{weight \% of aromatics}}{100} + (\delta_{\text{olefins}} - \delta_{\text{sats.}}) \times \frac{\text{weight \% of olefins}}{100}$$

where $\delta_{\text{arom.}}$ and δ_{olefins} are the average specific dispersions of the pure aromatics and pure olefins present in the mixture.

Since the values of the specific dispersion of the saturates are practically always 99 ± 1 and the contribution due to olefins is equal to 0.16 × bromine number, the weight per cent of aromatics in the mixture will be given by the equation

weight % of aromatics =

$$\frac{\delta_{\text{mixt.}} - 0.16 \times \text{bromine number} - 99}{\delta_{\text{arom.}} - 99} \times 100$$

The values of the specific dispersion for aromatics boiling in various selected cuts of the gasoline range are as follows:

° C.		
70–95	Benzene	190.2
95–122	Toluene	184.9
122–150	Xylenes and ethylbenzene	179.2
150–175	C_9 and C_{10} aromatics (av.)	175.0
175–200	C_{10} and C_{11} aromatics (av.)	171.0

Thole (*7*) and Tizard and Marshall (*8*) have studied the separation by fractionation of the lower boiling aromatics and recommended the cutting temperatures of 95°—i. e., 70° to 95°—and 122° C.—i. e., 95° to 122°. For most cases, however, the dispersion method will give results within the experimental error if the usual cutting temperatures of 100° C.—i. e., 70° to 100°—and 125° C.—i. e., 100° to 125°—are used. The analyst should select the correct temperatures after giving consideration to the efficiency of the fractionation column and to further type analysis, such as determination of C_6, C_7, C_8, and C_9 paraffins.

For such cuts, therefore, the weight per cent of aromatics may readily be calculated using the above equation, or more accurately by means of Table III, which takes into consideration any deviations from the straight-line relationship. For wider boiling cuts, values averaged from the above may be used.

Measurement of Dispersion

The dispersion of a liquid sample may be determined in the course of 0.5 to 1 minute on a standard Abbé refractometer simultaneously with the n_D determination. Daylight is used and the dispersion angle, Z, is read off the ring at the lower end of the tube (A, Figure 5) and converted to dispersion for the $H_\beta - H_\alpha$ lines by means of an equation supplied with each instrument. The procedure for taking readings recommended by the firm of C. Zeiss or the Bausch & Lomb Optical Company should be strictly adhered to.

The dispersions obtained on the Abbé refractometer vary within ±1 to 2 units if measured by an experienced observer. For accurate measurements the Pulfrich refractometer of C. Zeiss Co., Jena, is recommended. With this instrument the index of refraction may be measured for any desired wave length in the visible spectrum. Using a hydrogen-filled Geissler tube the $n_{H_\beta} - n_{H_\alpha}$ dispersion can be determined with an accuracy of ±0.1 to 0.2 unit. Since the dispersion is measured by difference (micrometric screw) it is more accurate than the absolute values of the indices.

After the density (Westphal balance, areometer, or pycnometer) and bromine number of the fraction are known, the aromatic content can be determined in a minute or two. Table III is used to convert the specific dispersion of the mixture, corrected for any olefinic content, directly into weight per cent of aromatics; in preparing this table consideration was given to the straight-line deviations.

The Abbé dispersion angles or Z values have to be converted into dispersions by means of the equation

$$\Delta_{H_\beta - H_\alpha} = nF - nC = (A + B\sigma) \times 10{,}000$$

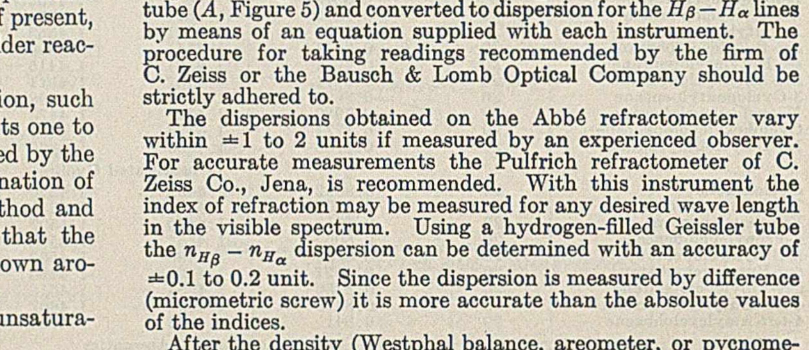

Figure 4. Specific Dispersion *vs.* Bromine Number for Unsaturates

Table III. Specific Dispersion, $\delta_{H_\beta - H_\alpha}$, of Gasoline and Naphtha Cuts

(Corrected to olefin-free basis)

Weight % of Aromatics	Benzene	Toluene	Xylenes and Ethylbenzene	C_3 and C_4 Alkylbenzenes	C_4 and C_5 Alkylbenzenes
	Cutting Temperatures				
	70–95° or 70–100° C.	95–122° or 100–125° C.	122–150° or 125–150° C.	150–175° C.	175–200° C.
0	98.0	99.0	99.0	99.0	99.0
1	98.9	99.8	99.8	99.8	99.7
2	99.7	100.6	100.6	100.5	100.4
3	100.6	101.4	101.3	101.3	101.2
4	101.4	102.2	102.1	102.0	101.9
5	102.3	103.0	102.9	102.8	102.6
6	103.1	103.9	103.7	103.6	103.3
7	104.0	104.7	104.5	104.3	104.0
8	104.8	105.5	105.2	105.1	104.8
9	105.7	106.3	106.0	105.8	105.5
10	106.5	107.1	106.8	106.6	106.2
11	107.4	107.9	107.6	107.4	106.9
12	108.2	108.8	108.4	108.1	107.6
13	109.1	109.6	109.2	108.9	108.4
14	110.0	110.4	110.0	109.6	109.1
15	110.8	111.3	110.8	110.4	109.8
16	111.7	112.1	111.5	111.2	110.5
17	112.6	112.9	112.3	111.9	111.2
18	113.4	113.8	113.1	112.7	112.0
19	114.3	114.6	113.9	113.4	112.7
20	115.2	115.4	114.7	114.2	113.4
21	116.0	116.2	115.5	115.0	114.1
22	116.9	117.1	116.3	115.7	114.8
23	117.8	117.9	117.1	116.5	115.6
24	118.7	118.7	117.9	117.2	116.3
25	119.6	119.6	118.7	118.0	117.0
26	120.5	120.4	119.4	118.8	117.7
27	121.4	121.2	120.2	119.5	118.4
28	122.3	122.1	121.0	120.3	119.2
29	123.2	122.9	121.8	121.0	119.9
30	124.1	123.7	122.6	121.8	120.6
31	125.0	124.5	123.4	122.6	121.3
32	125.9	125.4	124.2	123.3	122.0
33	126.8	126.2	125.0	124.1	122.8
34	127.7	127.1	125.8	124.8	123.5
35	128.6	127.9	126.6	125.6	124.2
36	129.5	128.7	127.4	126.4	124.9
37	130.4	129.6	128.2	127.1	125.6
38	131.3	130.4	129.0	127.9	126.4
39	132.2	131.3	129.8	128.6	127.1
40	133.1	132.1	130.6	129.4	127.8
41	134.0	133.0	131.4	130.2	128.5
42	134.9	133.8	132.2	130.9	129.2
43	135.8	134.7	133.0	131.7	130.0
44	136.7	135.5	133.8	132.4	130.7
45	137.6	136.4	134.6	133.2	131.4
46	138.5	137.3	135.4	134.0	132.1
47	139.4	138.1	136.2	134.7	132.8
48	140.3	139.0	137.0	135.5	133.6
49	141.2	139.8	137.8	136.2	134.3
50	142.2	140.7	138.6	137.0	135.0
51	143.1	141.6	139.4	137.8	135.7
52	144.0	142.4	140.2	138.5	136.4
53	145.0	143.3	141.0	139.3	137.2
54	145.9	144.1	141.8	140.0	137.9
55	146.8	145.0	142.7	140.8	138.6
56	147.8	145.9	143.5	141.6	139.3
57	148.7	146.7	144.3	142.3	140.0
58	149.6	147.6	145.1	143.1	140.8
59	150.5	148.4	145.9	143.8	141.5
60	151.5	149.3	146.7	144.6	142.2
61	152.4	150.2	147.5	145.4	142.9
62	153.4	151.1	148.3	146.1	143.6
63	154.3	151.9	149.1	146.9	144.4
64	155.3	152.8	149.9	147.6	145.1
65	156.2	153.7	150.7	148.4	145.8
66	157.2	154.6	151.5	149.2	146.5
67	158.1	155.5	152.3	149.9	147.2
68	159.1	156.3	153.1	150.7	148.0
69	160.0	157.2	153.9	151.4	148.7
70	160.9	158.1	154.7	152.2	149.4
71	161.9	159.0	155.5	153.0	150.1
72	162.8	159.9	156.3	153.7	150.8
73	163.8	160.7	157.1	154.5	151.6
74	164.7	161.6	157.9	155.2	152.3
75	165.7	162.5	158.8	156.0	153.0
76	166.7	163.4	159.6	156.8	153.7
77	167.6	164.3	160.4	157.5	154.5
78	168.6	165.1	161.2	158.3	155.2
79	169.5	166.0	162.0	159.2	155.9
80	170.5	166.9	162.8	159.8	156.6
81	171.5	167.8	163.6	160.6	157.3
82	172.4	168.7	164.4	161.3	158.0
83	173.4	169.6	165.3	162.1	158.8
84	174.4	170.5	166.1	162.8	159.5
85	175.4	171.4	166.9	163.6	160.2
86	176.3	172.2	167.7	164.4	160.9
87	177.3	173.1	168.5	165.1	161.6
88	178.3	174.0	169.3	165.9	162.4
89	179.2	174.9	170.2	166.6	163.1
90	180.2	175.8	171.0	167.4	163.8
91	181.2	176.7	171.8	168.2	164.5
92	182.2	177.6	172.6	168.9	165.2
93	183.2	178.5	173.5	169.7	166.0
94	184.2	179.4	174.3	170.4	166.7
95	185.2	180.4	175.1	171.2	167.4
96	186.2	181.3	175.9	172.0	168.1
97	187.1	182.2	176.7	172.7	168.8
98	188.1	183.1	177.6	173.5	169.6
99	189.1	184.0	178.4	174.2	170.3
100	190.1	184.9	179.2	175.0	171.0

Corrections to Be Added to Experimental Specific Dispersions of Mixtures with Change in Base Value of Saturated Hydrocarbon Mixture

Weight % of Aromatics	Base Value for Saturates				
	96.0	97.0	98.0	99.0	100.0
	Benzene				
0	+2.0	+1.0	0	−1.0	−2.0
10	+1.8	+0.9	0	−0.9	−1.8
20	+1.6	+0.8	0	−0.8	−1.6
30	+1.4	+0.7	0	−0.7	−1.4
40	+1.2	+0.6	0	−0.6	−1.2
50	+1.0	+0.5	0	−0.5	−1.0
60	+0.8	+0.4	0	−0.4	−0.8
70	+0.6	+0.3	0	−0.3	−0.6
80	+0.4	+0.2	0	−0.2	−0.4
90	+0.2	+0.1	0	−0.1	−0.2
100	0.0	0.0	0	0.0	0.0

Weight % of Aromatics	Base Value for Saturates				
	96.0	97.0	98.0	99.0	100.0
	Toluene and Higher				
0	+3.0	+2.0	+1.0	0	−1.0
10	+2.7	+1.8	+0.9	0	−0.9
20	+2.4	+1.6	+0.8	0	−0.8
30	+2.1	+1.4	+0.7	0	−0.7
40	+1.8	+1.2	+0.6	0	−0.6
50	+1.5	+1.0	+0.5	0	−0.5
60	+1.2	+0.8	+0.4	0	−0.4
70	+0.9	+0.6	+0.3	0	−0.3
80	+0.6	+0.4	+0.2	0	−0.2
90	+0.3	+0.2	+0.1	0	−0.1
100	0.0	0.0	0.0	0	0.0

where A and B are constants depending on the n_D and dispersion of the particular batch of glass used in the preparation of the refractometer's prism and σ is a function of Z.

Each Abbé refractometer is supplied with a table giving the values for these quantities; furthermore, the number of the dispersion table to be used with a particular instrument is always stamped in the lower right-hand corner of the index scale.

In order to convert the angle reading directly and immediately into dispersions, Table IV has been prepared. It takes the place of C. Zeiss dispersion table No. 30, and may be used for every refractometer having the number 30 on the lower right-hand corner of the index scale. Tables similar to Table IV can be calculated for any given pair of the A and B constants.

Results with Synthetic Mixtures

A number of synthetic mixtures containing varying amounts of aromatics, paraffins, naphthenes, and olefins were prepared and their n_D, n_{H_β}, n_{H_α}, d^t_4, Δ, δ, and bromine numbers (Francis' method) determined. Benzene, toluene, and a mixture of xylenes and ethylbenzene were taken as representative of aromatics. n-Heptane and 2,2,4-trimethylpentane, and cyclohexane and methylcyclohexane were chosen as representatives of the paraffins and naphthenes, respectively. The unsaturates used were 2-ethylhexene-1, 2-methylbutadiene-1,3 (isoprene), and 2-methylpentadiene-1,3. The properties of the pure hydrocarbons, as used by the authors, are given in Table I. All data, including both the Abbé (Zeiss No. 49,242) and Pulfrich refractometer (Zeiss No. N-59,956) measurements, are correlated in Tables V to IX. As can be seen, the accuracy of measurement with the Abbé instrument is sufficient for many practical purposes, such as control analysis. However, for more accurate analysis the Pulfrich instrument gives results to approximately ±1 per cent of the aromatic content.

Table IV. Dispersions,

(As a function of Z and n_D, in Z range 10 to 50 and

Z_{30}	1.350	1.360	1.370	1.380	1.390	1.400	1.410	1.420	1.430	1.440	1.450	1.460	1.470	1.480	1.490
10	522.3	520.1	517.8	515.3	512.7	509.8	507.0	504.0	501.0	497.7	494.5	491.0	487.4	483.7	479.9
11	513.8	511.6	509.4	506.9	504.4	501.6	498.9	496.0	493.0	489.8	486.7	483.3	479.8	476.3	472.5
12	504.3	501.8	499.7	497.3	494.8	492.5	489.5	486.7	483.8	480.8	478.0	474.7	471.4	467.9	464.3
13	494.1	492.7	490.0	487.7	485.3	482.7	480.2	477.4	474.6	471.7	468.8	465.6	462.4	459.1	455.6
14	483.3	481.4	479.3	477.2	474.8	472.3	469.9	467.3	464.6	461.8	459.0	455.9	452.8	449.6	446.3
15	471.9	470.0	468.1	466.0	463.7	461.4	459.0	456.5	453.9	451.2	448.6	445.6	442.7	439.7	436.5
16	459.9	458.1	456.2	454.2	452.1	449.8	447.5	445.1	442.7	440.1	437.6	434.8	432.0	429.1	426.1
17	447.2	445.5	443.7	441.8	439.7	437.6	435.5	432.2	430.9	428.4	426.0	423.4	420.7	418.0	415.2
18	434.2	432.6	430.9	429.1	427.1	425.1	423.1	420.9	418.7	416.4	414.2	411.7	409.2	406.7	404.0
19	420.6	419.0	417.4	415.7	413.9	412.0	410.1	408.1	406.0	403.9	401.8	399.4	397.1	394.7	392.2
20	406.3	404.9	403.4	401.8	400.1	398.3	396.5	394.6	392.7	390.7	388.8	386.6	384.5	382.3	380.0
21	391.7	390.4	389.0	387.5	385.9	384.2	382.6	380.8	379.1	377.2	375.5	373.5	371.5	369.5	367.4
22	376.8	375.6	374.3	372.9	371.4	369.9	368.4	366.8	365.2	363.5	361.9	360.1	358.3	356.5	354.6
23	361.3	360.1	358.9	357.7	356.4	355.0	353.6	352.1	350.7	349.2	347.7	346.1	344.5	342.9	341.2
24	345.8	344.7	343.6	342.5	341.3	340.0	338.8	337.5	336.2	334.9	333.6	332.1	330.7	329.3	327.8
25	329.9	329.0	328.0	327.0	325.9	324.8	323.7	322.5	321.4	320.2	319.1	317.9	316.7	315.4	314.1
26	313.7	312.9	312.0	311.1	310.2	309.2	308.3	307.3	306.3	305.3	304.4	303.3	302.3	301.3	300.2
27	297.3	296.5	295.8	295.0	294.2	293.4	292.6	291.7	290.9	290.1	289.4	288.5	287.7	286.9	286.0
28	280.8	280.1	279.5	278.9	278.2	277.5	276.9	276.2	275.6	274.9	274.3	273.7	273.1	272.4	271.8
29	264.3	263.8	263.3	262.7	262.2	261.7	261.2	260.6	260.2	259.7	259.3	258.8	258.4	258.0	257.6
30	247.8	247.4	247.0	246.6	246.2	245.8	245.5	245.1	244.8	244.5	244.3	244.0	243.8	243.6	243.4
31	231.3	231.0	230.7	230.5	230.2	229.9	229.8	229.6	229.4	229.3	229.3	229.2	229.2	229.2	229.2
32	214.8	214.7	214.5	214.3	214.2	214.1	214.1	214.0	214.0	214.1	214.3	214.3	214.5	214.8	215.0
33	198.3	198.3	198.2	198.2	198.2	198.2	198.4	198.5	198.7	198.9	199.2	199.5	199.8	200.3	200.8
34	181.9	181.9	182.0	182.1	182.2	182.4	182.7	182.9	183.3	183.7	184.2	184.7	185.3	185.9	186.6
35	165.7	165.8	166.0	166.2	166.5	166.8	167.3	167.7	168.2	168.8	169.5	170.1	170.9	171.8	172.7
36	149.8	150.1	150.4	150.7	151.1	151.6	152.2	152.7	153.4	154.1	155.0	155.9	156.9	157.8	159.0
37	134.3	134.7	135.1	135.5	136.0	136.6	137.4	138.1	138.9	139.8	140.9	141.9	143.1	144.3	145.6
38	118.8	119.2	119.7	120.3	121.0	121.7	122.6	123.4	124.4	125.5	126.7	127.9	129.3	130.7	132.2
39	103.9	104.4	105.0	105.7	106.5	107.4	108.4	109.4	110.5	111.8	113.1	114.5	116.1	117.7	119.4
40	89.3	89.9	90.6	91.4	92.3	93.3	94.5	95.6	96.9	98.3	99.8	101.4	103.1	104.9	106.8
41	75.0	75.8	76.6	77.5	78.5	79.6	80.9	82.1	83.6	85.1	86.8	88.6	90.5	92.5	94.6
42	61.4	62.2	63.1	64.1	65.3	66.5	67.9	69.3	70.9	72.6	74.4	76.3	78.4	80.5	82.8
43	48.4	49.3	50.3	51.4	52.7	54.0	55.5	57.0	58.7	60.6	62.6	64.6	66.9	69.2	71.6
44	35.7	36.7	37.8	39.0	40.3	41.8	43.5	45.1	46.9	48.9	51.0	53.2	55.6	58.1	60.7
45	23.7	24.8	25.9	27.2	28.7	30.2	32.0	33.7	35.7	37.8	40.0	42.4	44.9	47.5	50.3
46	12.3	13.4	14.7	16.0	17.6	19.3	21.1	22.9	25.0	27.2	29.6	32.1	34.8	37.6	40.5
47	1.5	2.7	4.0	5.5	7.1	8.9	10.8	12.8	15.0	17.3	19.8	22.4	25.2	28.1	31.2
48	...	...	...	...	...	...	1.5	3.5	5.8	8.2	10.6	13.3	16.2	19.3	22.5
49	...	...	...	...	...	...	...	...	...	...	1.9	4.7	7.8	10.9	14.3
50	...	...	...	...	...	...	...	...	...	...	...	...	0.2	3.5	6.9

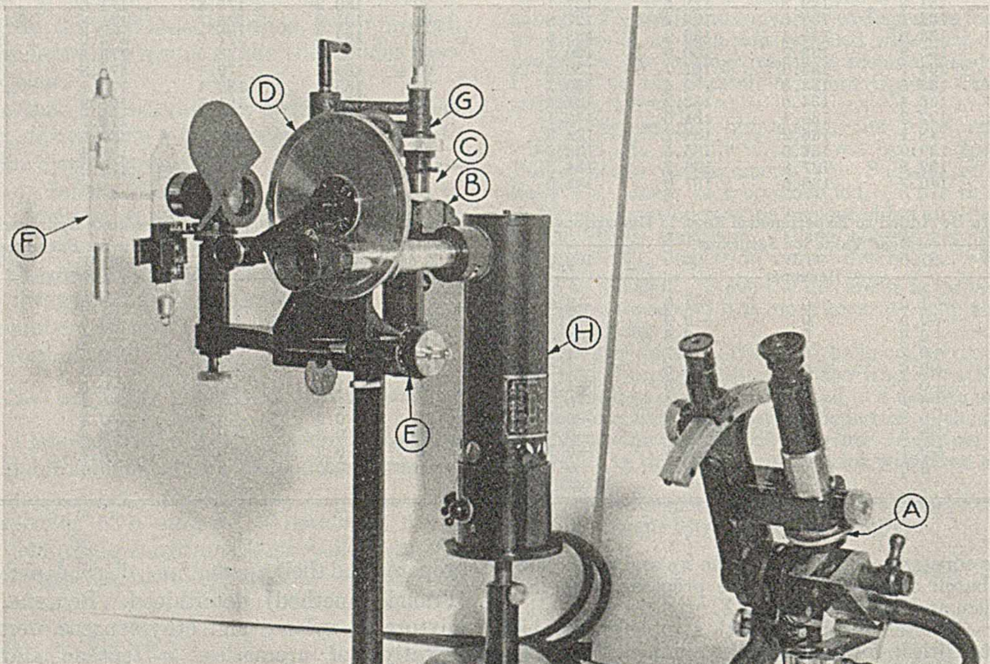

Figure 5. Pulfrich (*left*) and Abbé (*right*) Refractometers

A. Dispersion angle (Z) ring
B. Prism
C. Glass ring for sample
D. Graduated circle for measuring angle of light
E. Micrometric screw
F. Geissler tube
G. Constant-temperature device
H. Sodium lamp for measuring n_D

$\Delta_{\beta-\alpha}$, i. e. $(n_{H_\beta} - n_{H_\alpha})\cdot 10{,}000$

n_D 1.350 to 1.650. For C. Zeiss Dispersion Table 30)

Z_{30}	1.500	1.510	1.520	1.530	1.540	1.550	1.560	1.570	1.580	1.590	1.600	1.610	1.620	1.630	1.640	1.650
10	476.0	471.9	467.8	463.3	458.8	454.1	449.3	444.3	439.0	433.6	427.9	422.0	415.9	409.7	403.2	396.5
11	468.7	464.8	460.8	456.5	452.1	447.6	442.9	438.0	432.9	427.7	422.2	416.5	410.6	404.5	398.3	391.8
12	460.7	456.9	453.0	448.8	444.6	440.3	435.7	430.8	425.9	420.9	415.8	410.1	404.4	398.6	392.8	386.4
13	452.1	448.4	444.7	440.7	436.7	432.5	428.1	423.6	418.9	414.1	409.0	403.8	398.3	392.7	387.0	381.0
14	442.9	439.4	435.9	432.0	428.2	424.2	420.0	415.7	411.2	406.6	401.7	396.8	391.6	386.2	380.8	375.1
15	432.3	429.9	426.5	422.9	419.2	415.4	411.4	407.4	403.1	398.7	394.1	389.4	384.4	379.4	374.2	368.8
16	423.1	419.9	416.7	413.2	409.7	406.1	402.4	398.5	394.5	390.3	386.0	381.5	376.9	372.1	367.3	362.2
17	412.3	409.3	406.3	403.1	399.8	396.4	392.9	389.3	385.5	381.6	377.5	373.3	369.0	364.5	360.0	355.2
18	401.3	398.5	395.7	392.6	289.6	386.4	383.1	379.7	376.2	372.6	368.7	364.9	360.8	356.7	352.5	348.1
19	389.7	387.1	384.5	381.7	378.9	375.9	372.9	369.7	366.5	363.1	359.6	356.1	352.3	348.5	344.7	340.6
20	377.7	375.3	372.9	370.3	367.7	365.0	362.2	359.3	356.3	353.3	350.1	346.8	343.4	340.0	336.5	332.8
21	365.3	363.1	360.9	358.6	356.2	353.7	351.2	348.6	345.9	343.2	340.3	337.3	334.3	331.2	328.1	324.7
22	352.7	350.7	348.7	346.6	344.5	342.3	340.0	337.7	335.3	332.8	330.3	327.7	325.0	322.2	319.5	316.6
23	339.5	337.7	336.0	334.1	332.3	330.3	328.3	326.3	324.2	322.1	319.8	317.6	315.3	312.9	310.5	308.0
24	326.3	324.8	323.3	321.7	320.1	318.4	316.7	314.9	313.1	311.3	309.4	307.5	305.5	303.6	301.6	299.5
25	312.9	311.6	310.4	309.0	307.6	306.2	304.8	303.3	301.8	300.4	298.8	297.3	295.6	294.0	292.5	290.8
26	299.2	298.1	297.1	296.0	294.9	293.8	292.6	291.5	290.3	289.2	287.9	286.8	285.5	284.3	283.2	281.9
27	285.2	284.4	283.7	282.8	282.0	281.1	280.2	279.4	278.6	277.7	276.9	276.1	275.2	274.4	273.7	272.9
28	271.2	270.7	270.2	269.5	269.0	268.4	267.9	267.3	266.8	266.3	265.8	265.4	264.9	264.5	264.2	263.8
29	257.3	256.9	256.7	256.3	256.1	255.8	255.5	255.3	255.1	254.9	254.8	254.7	254.6	254.6	254.7	254.8
30	243.3	243.2	243.2	243.1	243.1	243.1	243.1	243.2	243.3	243.5	243.7	244.0	244.3	244.7	245.2	245.7
31	229.3	229.5	229.7	229.9	230.1	230.4	230.7	231.1	231.5	232.1	232.6	233.3	234.0	234.8	235.7	236.6
32	215.4	215.7	216.2	216.7	217.2	217.8	218.3	219.1	219.8	220.7	221.6	222.6	223.7	224.9	226.2	227.6
33	201.4	202.0	202.7	203.4	204.2	205.1	206.0	207.0	208.0	209.3	210.5	211.9	213.4	215.0	216.7	218.5
34	187.4	188.3	189.3	190.2	191.3	192.4	193.6	194.9	196.3	197.8	199.5	201.2	203.1	205.1	207.2	209.5
35	173.7	174.8	176.0	177.2	178.6	180.0	181.4	183.1	184.8	186.6	188.6	190.7	193.0	195.4	197.9	200.6
36	160.3	161.6	163.1	164.5	166.1	167.8	169.5	171.5	173.5	175.7	178.0	180.5	183.1	185.8	188.8	191.9
37	147.1	148.7	150.4	152.1	153.9	155.9	157.9	160.1	162.4	164.9	167.6	170.4	173.3	176.5	179.9	183.4
38	133.9	135.7	137.7	139.6	141.7	143.9	146.2	148.7	151.3	154.2	157.1	160.3	163.6	167.2	170.9	174.8
39	121.3	123.3	125.5	127.6	130.0	132.5	135.0	137.8	140.7	143.8	147.1	150.7	154.3	158.2	162.3	166.7
40	108.9	111.1	113.5	115.9	118.5	121.2	124.0	127.1	130.3	133.7	137.3	141.2	145.2	149.4	153.9	158.6
41	96.9	99.3	101.9	104.5	107.3	110.3	113.3	116.7	120.1	123.9	127.8	131.1	136.3	140.9	145.7	150.8
42	85.3	87.9	90.7	93.6	96.6	99.8	103.1	106.7	110.4	114.4	118.7	123.1	127.8	132.7	137.9	143.3
43	74.3	77.1	80.1	83.1	86.4	89.8	93.3	97.1	101.1	105.4	109.9	114.7	119.6	124.9	130.4	136.2
44	63.5	66.5	69.7	73.0	76.5	80.1	83.8	87.9	92.1	96.7	101.4	106.5	111.7	117.3	123.1	129.2
45	54.3	56.5	59.9	63.3	67.0	70.8	74.8	79.0	83.5	88.3	93.3	98.6	104.2	110.0	116.2	122.6
46	43.7	47.0	50.5	54.2	58.0	62.0	66.2	70.7	75.4	80.4	85.7	91.2	97.0	103.2	109.6	116.3
47	34.5	38.0	41.7	45.5	49.5	53.7	58.1	62.8	67.7	72.9	78.4	84.2	90.3	96.7	103.4	110.4
48	25.9	29.5	33.4	37.4	41.6	45.9	50.5	55.6	60.7	66.1	71.6	77.9	84.2	90.8	97.6	105.0
49	17.9	21.6	25.6	29.7	34.1	38.6	43.3	48.4	53.7	59.3	65.2	71.5	78.0	84.9	92.1	99.6
50	10.6	14.5	18.6	22.9	27.4	32.1	36.9	42.1	47.6	53.4	59.5	66.0	72.7	79.7	87.2	94.9

Table V. Benzene Series (No Olefins)

	No. 126	No. 66-A	No. 66-B	No. 66-Ç	No. 118-A	No. 119-A	No. 66-D
Weight %							
Benzene	0	11.89	30.21	53.73	54.11	52.22	78.69
n-Heptane	48.44	41.11	32.52	21.77	0	47.78	9.80
Cyclohexane	51.56	47.00	37.27	24.50	45.89	0	11.51
d_4^{20}	0.7270	0.7423	0.7650	0.7978	0.8244	0.7696	0.8391
By Abbé							
Z	.....	40.9	40.0	38.7	.....	.....	37.1
n_D^{20}	.....	1.4143	1.4284	1.4493	.....	.....	1.4754
Δ	.....	82.9	96.6	117.1	.....	.....	142.4
δ	.....	112	126	147	.....	.....	170
Benzene, % (from Table III)	.....	16	32	55	.....	.....	80
Deviation	.....	+4.1	+1.8	+1.3	.....	.....	+1.3
By Pulfrich							
n_D^{20}	1.4050	1.4142	1.4282	1.4493	1.4611	1.4365	1.4751
Δ	70.4	79.5	94.6	116.1	120.0	110.4	141.4
δ	96.8	107.1	123.7	145.5	145.5	143.4	168.5
Benzene, % (from Table III and corrections)	0	11.8	30.4	54.1	54.1	51.9	78.3
Deviation	0.0	−0.1	+0.2	+0.4	0.0	−0.3	−0.4

Straight-Line Deviations of Specific Dispersion *vs.* Concentration Relation

The deviation from a straight-line function of the specific dispersion *vs.* concentration relation in the benzene, toluene, and xylene series appears only when precision Pulfrich refractometer measurements are made. The Pulfrich experimental data were found to fit equations of the type:

$$\delta = A + BW + CW^2$$

where W represents the weight per cent of aromatics. The following equations were obtained by the least square method from the data of Tables I, V, and VI.

70° to 100° C. (benzene): $\delta = 96.9 + 0.8577W + 0.000744W^2$ (1)

100° to 125° C. (toluene): $\delta = 99.1 + 0.8076W + 0.000504W^2$ (2)

125° to 150° C. (xylenes and ethylbenzene): $\delta = 99.1 + 0.7822W + 0.000188W^2$ (3)

The average (±) deviations in weight per cent of aromatics are in the first two cases 0.2 and 0.1, respectively, and actual deviations are shown in the tables.

Comparison of the above equations shows that as the boiling range increases the equation approaches more closely a straight-line function.

The deviation of the specific dispersion from a straight line at the 50 per cent point is in each case 1.9, 1.3, and 0.5 unit, respectively. This rapid decrease indicates that as the number of side chains in the aromatic hydrocarbon increases—i. e., as its "paraffinicity" increases—more ideal solutions are produced. It seemed reasonable, therefore, to assume a straight-line relationship of δ and W in the boiling ranges 150° to 175° and 175° to 200° C. The equations covering these ranges are as follows:

150° to 175° C.: $\delta = 99 + 0.76W$ (4)

175° to 200° C.: $\delta = 99 + 0.72W$ (5)

The base value of 99 for paraffins and naphthenes is reasonable in view of existing literature data. The lower value (96.9) in Equation 1 is due to the fact that both cyclohexane and *n*-heptane as used in these mixtures have specific dispersions slightly lower than 99. In typical gasoline analysis a

TABLE VI. TOLUENE SERIES (NO OLEFINS)

	No. 127	No. 68-A	No. 68-B	No. 68-C	No. 68-D	No. 144 (Xylenes)
Weight %						
Toluene	0	12.05	27.01	54.77	77.71	0
o-Xylene	0	0	0	0	0	10.59
m-Xylene	0	0	0	0	0	12.18
p-Xylene	0	0	0	0	0	13.16
Ethylbenzene	0	0	0	0	0	13.98
2,2,4-Trimethylpentane	49.65	42.51	34.33	21.17	10.59	24.87
Methylcyclohexane	50.35	45.44	38.66	24.06	11.70	25.22
d_4^{20}	0.7294	0.7434	0.7606	0.7983	0.8305	0.7915
By Abbé						
Z	.....	40.9	40.2	38.7	37.4	.....
n_D^{20}	.....	1.4160	1.4275	1.4510	1.4728	.....
Δ	.....	83.2	93.8	117.4	137.8	.....
δ	.....	112	123	147	166	.....
Toluene, % (from Table III)	.....	16	29	57	79	.....
Deviation	.....	+3.9	+2.0	+2.3	+1.3	.....
By Pulfrich						
n_D^{20}	1.4070	1.4158	1.4275	1.4510	1.4728	1.4477
Δ	72.3	80.9	92.2	115.8	136.9	109.7
δ	99.1	108.7	121.2	145.1	164.8	138.6
Toluene, % (from Table III and corrections)	0.0	11.9	27.0	55.0	77.5	.....
Deviation	0.0	−0.2	0.0	+0.2	−0.2	.....

TABLE VII. AROMATIC-FREE OLEFIN SERIES

	No. 75-A	No. 75-B	No. 81-C	No. 81-D
Weight %				
n-Heptane	46.25	33.59	24.66	12.79
Cyclohexane	44.66	32.42	23.66	12.27
2-Ethylhexene-1	9.09	33.99	51.68	74.94
d_4^{20}	0.7271	0.7324	0.7363	0.7420
Bromine No. (experimental)	11.7	42.5	64.6	93.4
By Abbé				
Z	41.2	40.9	40.8	40.6
n_D^{20}	1.4053	1.4093	1.4122	1.4164
Δ	77.5	82.2	83.8	87.1
δ	107	112	114	117
δ corrected	105	105	104	102
By Pulfrich				
n_D^{20}	1.4056	1.4092	1.4129	1.4164
Δ	71.9	76.9	80.0	83.5
δ	98.9	105.0	108.6	112.5
δ corrected	97.0	98.2	98.3	97.5
Deviation from base value of δ = 96.8	+0.2	+1.4	+1.5	+0.7

base value of 98 seems to be preferable and in accurate analysis it may be actually determined, as described below.

Table III, which is recommended for use in the analysis of gasolines, was constructed from the above equations by calculating the proportional change when the base value of the saturates is changed. For example, in the case of benzene the new specific dispersion of the mixture with 98 as the base was calculated from the following equation:

$$\delta_{\text{new mixt.}} = \left(\frac{\delta_{\text{old mixt.}} - 96.9}{190.1 - 96.9}\right)(190.1 - 98) + 98$$

It is reasonable to assume that the same deviation from a straight line will hold also, in first approximation, for mixtures of paraffins and naphthenes, particularly in natural gasolines and naphthas where possible individual constitutional effects are obliterated by the numerous other constituents.

Corrections are also given in Table III to be added to the values with a change in the base value. These tables become useful if one desires to determine the actual base value for the saturated mixture by removing the aromatics and unsaturates with sulfuric acid, sulfur dioxide, or by other methods. This procedure, however, is necessary only if very accurate analysis in the low aromatic concentration range is desired.

Selection of Specific Dispersion of Individual Aromatic Cuts

In Table X a comparison of specific dispersion values of benzene, toluene, ethylbenzene, and the xylenes by different authors is given. The results are in fair agreement and in calculations preference was given the authors' values since the purity of their compounds is known and, particularly, the data were corrected to their standard temperature of 20° C.

The value of 179.2 for the pure aromatics in the case of the xylenes and ethylbenzene was obtained by making a weighted average of the values for the four isomers.

To arrive at a reasonable value for the specific dispersion of the pure aromatics in the boiling ranges 150° to 175° and 175° to 200° C., existing literature data (*3, 11*) were averaged for each temperature range and plotted (Figure 1) against the average boiling point. This averaging was done in view of discrepancies existing even on the same compounds as reported by different authors. The result indicates a straight-line relation at least for the lower boiling ranges, and in view of the above-mentioned discrepancies and also the relatively high average value for the range 200° to 225° C., a straight line was assumed to continue through the ranges 150° to 200° C. The values of 175 and 171 at 162.5° and 187.5° C., respectively, were then used and Equations 4 and 5 calculated. The accuracy of the method is not affected as much as might be expected by the improper selection of these two values, since a variation of 4 units in the specific dispersion of the pure aromatic in the highest boiling fraction, where the greatest error would be encountered, results in an error of only 3 per cent aromatics at the 50 per cent aromatic point and correspondingly less at lower concentrations.

Literature data on the dispersions of the higher boiling aromatics are highly erratic and additional accurate measurements on these compounds are very desirable.

Effect of Double Bond and Relation between Specific Dispersion and Unsaturation

The effect of increasing double bond concentration on specific dispersion is shown in Figure 3, which is based on data obtained with a mixture of 2-ethylhexene-1, *n*-heptane, and cyclohexane and correlated in Table VII. The bromine numbers were determined by the Francis method (*2*). As will be noted, the points fall on a straight line.

The general relation is illustrated in Figure 4. Here the specific dispersion increments—i. e., the increase in the specific dispersion above the value for the saturated hydrocarbon—of mono- and diolefins, straight-chain and cyclic, are plotted against the bromine number. These data are taken from the literature values of Ward and Kurtz (Table XI) and the authors' Table I. Theoretical bromine numbers and average values for the specific dispersion increment were used. (A discussion as to whether the Francis or other bromine method is an accurate measure of unsaturation or should be replaced by other methods is outside the scope of this paper and will be discussed in a future publication.)

In view of these considerations and the uncertainty of the

Table VIII. Benzene Series Containing Olefins

	No. 70-A	No. 70-B	No. 70-C	No. 70-D	No. 71-A	No. 71-B	No. 71-C	No. 71-D
Weight %								
Benzene	10.76	27.16	49.53	72.89	8.67	21.70	38.60	56.92
n-Heptane	37.21	29.24	20.07	9.08	29.97	23.35	15.64	7.09
Cyclohexane	42.54	33.51	22.59	10.66	34.26	26.77	17.60	8.32
2-Ethylhexene-1	9.49	10.09	7.81	7.37	27.10	28.18	28.16	27.67
d_4^{20}	0.7427	0.7628	0.7935	0.8309	0.7437	0.7602	0.7824	0.8108
Bromine No. (experimental)	11.8	12.9	8.8	9.3	34.1	35.3	34.4	34.9
By Abbé								
Z	40.9	39.9	38.7	37.2	40.7	40.0	39.0	37.9
n_D^{20}	1.4148	1.4274	1.4466	1.4704	1.4158	1.4260	1.4402	1.4579
Δ	82.8	98.1	116.8	136.4	85.7	96.4	111.9	129.0
δ	111	128	147	164	115	127	143	159
δ corrected	109	126	146	162	110	121	137	153
Benzene, % (from Table III)	13	32	54	71	14	27	44	62
Deviation	+2.2	+4.8	+4.5	−1.9	+5.3	+5.3	+5.4	+5.1
By Pulfrich								
n_D^{20}	1.4145	1.4274	1.4464	1.4700	1.4156	1.4259	1.4401	1.4575
Δ	80.3	93.5	113.1	137.1	81.9	92.3	107.0	124.8
δ	108.2	122.6	142.5	165.0	110.1	121.4	136.8	153.9
δ corrected	106.3	120.5	141.1	163.5	104.7	115.8	131.3	148.3
Benzene, % (from Table III and corrections)	10.9	26.5	49.4	73.0	9.1	21.7	38.8	57.1
Deviation	+0.1	−0.7	−0.1	+0.1	0.4	0.0	+0.2	+0.2

Table IX. Toluene Series Containing Olefins

	No. 72-B	No. 72-D	No. 73-B	No. 73-D	No. 80-A	No. 80-B	No. 80-C	No. 80-D
Weight %								
Toluene	24.50	71.48	20.09	56.67	75.00	49.90	26.73	88.60
2,2,4-Trimethylpentane	31.14	9.74	25.54	7.72	0	0	0	0
Methylcyclohexane	35.08	10.76	28.76	8.54	0	0	0	0
2-Ethylhexene-1	9.28	8.02	25.61	27.07	25.00	50.10	73.27	11.40
d_4^{20}	0.7603	0.8236	0.7580	0.8066	0.8338	0.8033	0.7767	0.8513
Bromine No. (experimental)	11.5	9.7	32.5	33.6	30.9	62.8	91.0	14.1
By Abbé								
Z	40.3	37.5	40.0	38.2	37.2	38.4	39.3	36.6
n_D^{20}	1.4270	1.4681	1.4258	1.4574	1.4748	1.4552	1.4384	1.4864
Δ	93.9	136.1	96.4	124.9	140.9	121.7	106.3	150.5
δ	123	165	127	155	169	152	137	177
δ corrected	121	163	122	150	164	142	122	175
Toluene, % (from Table III)	27	76	28	61	77	52	28	89
Deviation	+2.5	+4.5	+7.9	+4.3	+2.0	+2.1	+1.3	+0.4
By Pulfrich								
n_D^{20}	1.4268	1.4680	1.4258	1.4573	1.4748	1.4549	1.4382	1.4863
Δ	91.8	132.3	91.1	122.0	139.1	120.3	104.5	150.0
δ	120.7	160.6	120.2	151.3	166.8	149.7	134.5	176.1
δ corrected	118.9	159.0	115.0	145.9	161.9	139.7	119.9	173.8
Toluene, % (from Table III and corrections)	24.1	70.9	19.5	56.0	74.2	48.9	25.2	87.8
Deviation	−0.4	−0.6	−0.6	−0.7	−0.8	−1.0	−1.5	−0.8

purity of the compounds, the straight-line relation seems reasonable. The agreement seems to be better with the olefins boiling in the gasoline range—i. e., bromine numbers 114 to 228. The slope of the lines of Figures 3 and 4 is approximately 0.16. The correction factor for olefins, diolefins, and unsaturated cyclics would therefore be equal to 0.16 × bromine number and the corrected specific dispersion to be used in connection with Table III would then be:

$$\delta_{\text{cor.}} = \delta_{\text{mixt.}} - 0.16 \times \text{bromine number}$$

For testing the above principle, a number of synthetic samples were made by adding 2-ethylhexene-1 to various mixtures of benzene, *n*-heptane, and cyclohexane, and toluene, 2,2,4-trimethylpentane, and methylcyclohexane. The results are given in Tables VIII and IX. The agreement is in general very good with the maximum deviation of ±1.5 per cent aromatics and average (±) deviations much less.

Additional data on the dispersions of unsaturates whose purity has been checked just previous to the dispersion measurement are very desirable in order to establish a more exact correction factor for these classes of compounds.

In general, the dispersion method is more accurate for mixtures high in aromatics and low in olefins than for the reverse case.

Analysis of Mixtures Containing Conjugated Diolefins

Conjugated diolefins have substantially higher specific dispersions than the unconjugated compounds, as can be seen from Table XII. Traces of conjugated diolefins will not appreciably affect the accuracy of aromatic determinations.

Table X. Specific Dispersion of Aromatics at 20° C.

Reference	Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
5	189.3	184.8	175.9	180.1	181.9	178.3
6	189.0	185.0	176.0	181.0	183.0	183.0
G. W.	190.2	184.9	174.7	179.7	181.3	181.9

Fortunately, mixtures containing substantial quantities of conjugated diolefins are comparatively rare, since they are produced under drastic temperature conditions. Practically, therefore, in a series of routine samples from a common source, usually only one representative sample will have to be checked for their presence.

The same applies to an even greater degree to aromatic olefins of the styrene type which have high specific dispersions (for instance styrene $\Delta^{20°} = 237.5$, $\delta^{20°} = 262.0$) in view of the exalting effect of an aromatic double bond in conjugation with an aliphatic double linkage.

If conjugated diolefins are present in large amounts, they have to be eliminated from the sample in order not to affect the determination of aromatics. This can be readily achieved by means of the Diels-Alder reaction with maleic anhydride; the latter forms addition compounds of the type

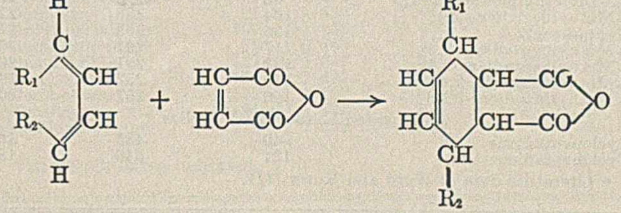

TABLE XI. SPECIFIC DISPERSION OF UNSATURATES

Hydrocarbon	N. B. P. ° C.	Theoretical Bromine No.	δ[a]	δ sat.	$\delta_{unsat.} - \delta_{sat.}$	
		Monoolefins				
Pentene-2 (*cis*)	36	227.9	134	97.9	36	
2-Methylbutene-2	38	227.9	135	98.3	37	Av. 36.5
4-Methylpentene-1	54	189.9	124	99.2	25	
3-Methylpentene-2 (*cis*)	66	189.9	130	96.9	33	
3-Methylpentene-2 (*trans*)	68	189.9	130	96.9	33	
2-Methylpentene-2	67	189.9	130	99.2	31	
Hexene-2	68	189.9	132	98.6	33	Av. 31
2,4-Dimethylpentene-2	83	162.8	125	98.7	26	
3-Ethylpentene-2	95	162.8	126	96	30	
Heptene-1	95	162.8	123	98.6	24	Av. 27
3-Ethylhexene-3	119	142.4	123	99	24	
4-Methylheptene-3	119	142.4	125	99	26	
2-Propylpentene-1	119	142.4	124	97.5	26	
Octene-1	124	142.4	119	98.2	21	
Octene-2	...	142.4	121	98.2	23	Av. 24
3-Ethylheptene-3	142	126.6	121	96	25	Av. 25(?)
2,7-Dimethyloctene-*x*	160	113.9	119	99	20	
4-Propylheptene-3	161	113.9	120	99[b]	21	
Decene-1	163	113.9	118	100	18	Av. 20
4-Propyldecene-3	221	87.7	116	98	18	
5-Butylnonene-3	85[b]	87.7	115	97	18	Av. 18
Cetene	274	71.2	108	98	10	
3-Ethyltetramethyldecene-2	144[b]	71.2	110	99[b]	11	
2-Methylpentamethyldecene-1	...	71.2	107	99[b]	8	Av. 10
		Diolefins (Unconjugated)				
2,6-Dimethylheptadiene-*x*,*x*	144	257	140	99[c]	41	
2,6-Dimethylheptadiene-1,*x*	144	257	143	99[c]	44	Av. 43
2,6-Dimethyloctadiene-*x*,*x*	163	231	135	97	38	
2,6-Dimethyloctadiene-*x*,*x*	...	231	140	97	43	Av. 41
		Unsaturated Cyclics				
Cyclohexene	83	194.6	119	96	23	Av. 23
1,1-Dimethylcyclohexene-3	120	145.1	116	96[c]	20	
1,2-Dimethylcyclohexene-3 and 4	125	145.1	114	96[c]	18	
1,3-Dimethylcyclohexene-3	125	145.1	119	96[c]	23	
1,3-Dimethylcyclohexene-4	127	145.1	122	96[c]	26	
1,3-Dimethylcyclohexene-5	127	145.1	119	96[c]	23	
1,4-Dimethylcyclohexene-1	127	145.1	117	96[c]	21	
1-Ethylcyclohexene-1	136	145.1	117	96[c]	21	
1,2-Dimethylcyclohexene-1	136	145.1	121	96[c]	25	Av. 22
1,1,2-Trimethylcyclohexene-4	139	128.7	118	96[c]	22	
1,3-Dimethyl-2-ethylcyclopentene-1	140	128.7	120	96[c]	24	
1,1,4-Trimethylcyclohexene-3	140	128.7	117	96[c]	21	
1,3,5-Trimethylcyclohexene-*x*	140	128.7	121	96[c]	25	
1,2,5-Trimethylcyclohexene-4	145	128.7	117	96[c]	21	
1,1,2-Trimethylcyclohexene-2	149	128.7	117	96[c]	21	
1,2,3-Trimethylcyclohexene-4	150	128.7	120	96[c]	24	
1,2-Diethylcyclopentene-*x*	152	128.7	116	96[c]	20	
1-Isopropylcyclohexene-1	156	128.7	116	96[c]	20	Av. 22
1-Methyl-2,5-diethylcyclopentene-1	164	115.6	119	96[c]	23	
1,2,4,5-Tetramethylcyclohexene-1	166	115.6	120	96[c]	24	
1-Methyl-4-isopropylcyclohexene-3	169	115.6	116	96[c]	20	Av. 22
1,2,5-Triethylcyclopentene-1	182	104.9	116	96[c]	20	Av. 20
1,3,4-Trimethyl-1-isopropylcyclohexene-3	78[b]	96	112	96[c]	16	Av. 16

[a] δ values from Ward and Kurtz (*11*).
[b] At 10 mm.
[c] Assumed.

TABLE XII. SPECIFIC DISPERSION OF CONJUGATED DIOLEFINS[a]

Hydrocarbon	N. B. P., ° C.	Theoretical Bromine No.	$\delta_{\beta-\alpha}$
	Conjugated Diolefins		
2-Methylbutadiene-1,3 (isoprene)	34.6	470	225
Pentadiene-1,3	43	470	243
2,3-Dimethylbutadiene-1,3	70	389	200
2-Methylpentadiene-2,4	76	389	226
2-Methylpentadiene-1,3	76	389	226
Hexadiene-2,4 (low boiling)	76	389	222
3-Methylpentadiene-1,3	78	389	225
Hexadiene-2,4 (high boiling)	79	389	232
2,3-Dimethylpentadiene-1,3	93	333	208
2-Methylhexadiene-2,4	104	333	226
Heptadiene-2,4	105	333	214
2-Methylheptadiene-3,5	117	291	206
4-Methylheptadiene-2,4	132	291	200
7-Methyloctadiene-2,4	149	257	197
4-Methyloctadiene-3,5	150	257	204
	Conjugated Unsaturated Cyclics		
Cyclopentadiene	40	485	164
Cycloheptadiene-1,3	121	340	185

[a] Literature data of Ward and Kurtz (*11*).

The reaction has already been applied for the removal, identification, or quantitative determination (butadiene-1,3) of conjugated diolefins in hydrocarbon mixtures (*5*, *6*, *9*).

The authors found in a preliminary investigation that the complete removal may usually be effected by heating the sample with 20 to 30 weight per cent of maleic anhydride in a sealed tube for 1 hour at 95° to 100° C. The procedure was to seal a 5- to 15-cc. sample in a test tube cooled by solid carbon dioxide and containing the anhydride and then heating it in a boiling water bath. After the reaction, the test tube was cooled in solid carbon dioxide, its tip broken off, and the whole tube slid down into a small distilling flask whence the total liquid content was distilled over into a trap cooled by solid carbon dioxide.

A decrease in bromine number of a sample after maleic anhydride treatment is a simple and definite criterion for the presence of conjugated diolefins and in all doubtful cases

TABLE XIII. MIXTURES CONTAINING CONJUGATED DIOLEFINS

	Experiment 1			Experiment 2				Experiment 3				Experiment 4		
	Diolefin-containing mixture No. 78-B	After maleic anhydride treatment	Original or diolefin-free mixture No. 71-D	Diolefin-containing mixture No. 78-D	After maleic anhydride treatment First	After maleic anhydride treatment Second	Original or diolefin-free mixture No. 72-D	Diolefin-containing mixture No. 77-B	After maleic anhydride treatment First	After maleic anhydride treatment Check	Original or diolefin-free mixture No. 71-C	Diolefin-containing mixture No. 77-A	After maleic anhydride treatment	Original or diolefin-free mixture No. 71-C
Weight %														
Aromatics														
Benzene	44.93	60	56.92	0	......	......	0	30.63	42	42	38.60	29.75	41	38.60
Toluene	0	......	0	65.23	70	69	71.48	0	......	......	0	0	.....	0
Paraffins														
n-Heptane	5.60	......	7.09	0	......	......	0	12.41	......	......	15.64	12.05	.....	15.64
2,2,4-Trimethylpentane	0	......	0	8.89	......	......	9.74	0	......	......	0	0	.....	0
Naphthenes														
Cyclohexane	6.57	......	8.32	0	......	......	0	13.97	......	......	17.60	13.56	.....	17.60
Methylcyclohexane	0	......	0	9.82	......	......	10.76	0	......	......	0	0	.....	0
Olefins														
2-Ethylhexene-1	21.83	......	27.67	7.32	......	......	8.02	22.34	......	......	28.16	21.71	.....	28.16
Conjugated diolefins														
2-Methylbutadiene-1,3	0	......	0	0	......	......	0	10.43	......	......	0	22.93	.....	0
2-Methylpentadiene-1,3	21.07	......	0	8.74	......	......	0	10.22	......	......	0	0	.....	0
d_4^{20}	0.7888	0.8148	0.8108	0.8138	0.830	0.8284	0.8326	0.7640	0.7838	0.7812	0.7824	0.7559	0.782	0.7824
n_D^{20}	1.4550	1.4586	1.4579	1.4661	1.4678	1.4660	1.4681	1.4376	1.4394	1.4380[a]	1.4402	1.4328	1.438	1.4402
Bromine No. (experimental)	97.5	32.3	34.9	36.3	9.4	9.1	9.7	97.0	30.2	36.3	34.4	109.1	40.7	34.4
Z	37.2	37.9	37.9	37.3	37.7	37.6	37.5	38.3	39.0	39.0	39.0	38.4	39.0	39.0
Δ (Abbé)	138.6	129.2	129.0	138.4	133.1	134.3	136.1	121.1	111.7	111.5	111.9	119.1	111.5	111.9
δ (Abbé)	175.7	159	159	170	163	162	165	159	143	143	143	158	143	143

[a] Actual weight per cent of material (diolefin) removed was 23% (theory 21%).

such a check is recommended; this difference in bromine number before and after treatment also gives the weight per cent of conjugated diolefins in the sample.

Results obtained by the maleic anhydride method are correlated in Table XIII. Mixtures of paraffins, naphthenes, olefins, and aromatics were prepared with the conjugated diolefins—isoprene and/or 2-methylpentadiene-1,3.

It can be seen by comparing the bromine number and other properties of the middle column of each experiment with the corresponding values of the original diolefin-free mixture that the diolefins have been practically completely removed. The aromatic content of the treated mixture, as determined by the Abbé refractometer, is in excellent accord with that of the original or diolefin-free mixture.

A repetition of the treatment, as shown in experiment 2, does not change, within experimental error, either the bromine number or the specific dispersion.

In experiment 3 a check was run and also the weight per cent of diolefin removed was determined directly by the increase in weight of the anhydride. Again full agreement with the first determination and the requirement of theory is observed.

Still further work on synthetic mixtures and conjugated diolefinic gasolines is desirable.

Effect of Oxygen, Sulfur, Nitrogen, and Halogen Compounds on Accuracy of Method

The present method is recommended for pure hydrocarbon mixtures, and tests for other elements should be made if suspected. However, since oxygen, sulfur, nitrogen, and halogen

TABLE XIV. OXYGEN, NITROGEN, SULFUR, AND HALOGEN COMPOUNDS

	N. B. P. ° C.	d_4^{20}	$n_D{}^a$	$\Delta_{H_\beta - H_\alpha}$	δ
Oxygen Compounds					
Methyl alcohol	64.5	0.792	1.329	54	68.1
Ethyl alcohol	78.5	0.7893	1.361	61	77.2
n-Propyl alcohol	97.8	0.804	1.386	66	82.0
n-Heptyl alcohol	175.8	0.819	1.425	74	90.4
Ethylene oxide	10.7	0.887^7	1.3597^7	58^7	65.3^7
Ethyl ether	34.5	0.714	1.3526	61	85.4
n-Propyl ether	89	0.747	1.3807	66	88.3
Phenol	182	1.057^{41}	1.5425^{41}	189^{41}	178.8^{41}
Benzyl alcohol	205.8	1.046	1.5399	173	165.3
o-Cresol	190.8	1.051	1.547	185	176.0
Furan	31	0.937	1.4216	113	120.5
2,5-Dimethyl furan	94	0.888	$1.4351^{21.6}$	114	128.3
Nitrogen Compounds					
Methyl cyanide	82	0.783	1.3474	58	74.0
Ethyl cyanide	97.1	0.783	1.3664	60	76.6
n-Propylamine	48.7	0.719	1.389	74	102.9
n-Butylamine	76	0.740	1.401	75	101.3
Triethylamine	89.5	0.728	1.401	81	111.2
Aniline	184.4	1.022	1.5863	249	243.6
Benzylamine	184	0.980	1.5440	175	178.5
Methylaniline	195.7	0.986	1.5714	249	252.5
Pyridine	115.3	0.982	1.509	163	165.9
Piperidine	105.8	0.860	1.4530	89	103.4
Sulfur Compounds					
Ethyl mercaptan	34.7	0.839	1.4306	102	121.5
Isobutyl mercaptan	88	0.836	1.4386	97	116.0
Isoamyl mercaptan	129.5	0.835	1.4412	91	108.9
Diethyl sulfide	91.6	0.837	1.4425	99	118.5
Diethyl disulfide	153	0.993	1.5063	130	130.9
Thiophene	84	1.065	1.5285	173	162.4
Thiophenol	168.69	1.074^{23}	1.5861^{23}	231^{23}	215.6^{23}
Halogen Compounds					
Carbon tetrachloride	76.8	1.595	1.4607	97	60.8
Chloroform	61.2	1.489	1.4467	89	59.7
n-Butyl bromide	101.6	1.275	1.4398	89	69.8
n-Butyl chloride	78	0.884	1.4015	71	80.3
n-Butyl iodide	127	1.617	1.5001	140	86.5
Bromobenzene	156.2	1.497	1.560	193	128.9
Chlorobenzene	132.1	1.107	1.525	172	155.3
Iodobenzene	188.6	1.832	1.621	253	138.1
o-Dichlorobenzene	179	1.298	1.549	176	135.5

[a] At 20° C. unless indicated.

compounds in small amounts are always possible constituents of natural and to a less extent of refined gasolines and naphthas, it is worth while to know the effect these would exert upon this method of analysis.

In Table XIV are listed a number of organic compounds containing the above constituents. These data were taken from the International Critical Tables. A survey of this table shows the specific dispersion to bear a similar relation to the carbon skeleton as found in hydrocarbons—for example, the specific dispersions of the phenols (176 to 179), thiophenol (216), and anilines (243 to 252) are much higher than the aliphatic alcohols (68 to 82), mercaptans (109 to 122), and alkylamines (101 to 111). That aromaticlike, heterocyclic systems have substantially higher specific dispersions than the saturated systems is well brought out by comparison of pyridine (166), thiophene (162), and furan (121), with piperidine (103), diethyl sulfide (119), and ethyl ether (85), respectively. (The two latter compounds may be taken as the closest analogies to tetrahydrothiophene and tetrahydrofuran, for which data are lacking.)

In general, the specific dispersions are of the same order of magnitude as similar types of hydrocarbons and none are exceptionally high. Practically, it may be expected that paraffinic and naphthenic gasolines will contain mainly aliphatic, oxygen, sulfur, nitrogen, or halogen derivatives, while aromatic gasolines will, correspondingly, contain aromatic or heterocyclic derivatives of these elements. It would be logical to consider the latter as "aromatics," just as any unsaturated oxygen, sulfur, nitrogen, or halogen compounds will be determined as "unsaturates." In view of this, and the fact that when present in gasolines the compounds are present in only small quantities (less than 1 to 2 per cent) it may safely be concluded that they will not affect the accuracy of the method.

A simple calculation shows that 0.1 per cent of sulfur, in the form of ethyl mercaptan, monosulfide, or disulfide, will raise the determined amount of benzene in a 25.0 weight per cent mixture with saturated hydrocarbons by 0.04, 0.06, and 0.12 weight per cent, respectively. The same amount of sulfur in the form of thiophenol (0.35 weight per cent) will raise the benzene content by 0.37 weight per cent, practically in complete agreement with the total aromatic ring content.

In general, oxygen compounds will lower and nitrogen and sulfur compounds will raise the specific dispersion of hydrocarbon mixtures.

TABLE XV. TEMPERATURE COEFFICIENTS

	$\frac{dn_D}{dt}$	$\frac{dn_{H\beta}}{dt}$	$\frac{dn_{H\alpha}}{dt}$	$\frac{d\Delta}{dt}$	$\frac{d\delta}{dt}$
Benzene	-0.0_3618	-0.0_3635	-0.0_3611	−0.2482	−0.051
Toluene	-0.0_3529	-0.0_3540	-0.0_3519	−0.2107	−0.048
n-Heptane	-0.0_3462	-0.0_3469	-0.0_3458	−0.1095	−0.037
2,2,4-Trimethylpentane	-0.0_3465	-0.0_3476	-0.0_3465	−0.1070	−0.031
Cyclohexane	-0.0_3501	-0.0_3505	-0.0_3494	−0.1163	−0.034
Methylcyclohexane	-0.0_3462	-0.0_3466	-0.0_3454	−0.1135	−0.039

Effect of Temperature on Dispersion and Specific Dispersion

The effect of temperature on specific dispersion is small and has usually been disregarded by previous workers, but for precision work it has to be taken into consideration. The authors have determined the specific dispersions of different types of hydrocarbons at 20° and 80° C. (see Table I). The calculated temperature coefficients of both the dispersion and specific dispersion are collected in Table XV.

The paraffins and naphthenes have dispersion temperature coefficients about one half that of the aromatics—i. e., approximately 0.11 and 0.23, respectively. The values for the specific dispersion temperature coefficient are also higher for the aromatics, although the difference is not so marked as in the case of the dispersion coefficients.

It is now possible accurately to convert dispersions and specific dispersions measured at some other temperature to the authors' standard temperature of 20° C.

As a first approximation, which is substantiated by unpublished data on high boiling compounds, the specific dispersion decreases linearly with temperature over this temperature range.

When an Abbé refractometer is used for the measurements at about room temperature (20° to 30°), it is not necessary to make the temperature correction, since the error in the measurement is greater than the correction. However, when Pulfrich measurements are made, it is advisable to make this correction. All measurements as given in the authors' tables were corrected on the above data.

TABLE XVI. COMPARISON OF SULFURIC ACID ABSORPTION AND DISPERSION METHODS OF ANALYSIS

Gasoline and Naphtha Sample (Bromine No. 0.0)	Weight Per Cent of Aromatics	
	By H_2SO_4	By specific dispersion
1	12	8
2	30	28
3	34	28
4	21	21
5	33	30

Results with Gasolines and Naphthas

A critical comparison of the accuracy and reliability of this method with other methods of aromatic determination will be made in another paper. However, a comparison with the most commonly used method—namely, extraction with concentrated 96 per cent sulfuric acid—is important and is shown in Table XVI.

The sulfuric acid method is at best reliable only for olefin-free mixtures. In the presence of olefins, as has been shown by Ipatieff and Pines (*4*), serious complications (alkylation of aromatics, polymerization, and paraffin formation) occur. In view of this, gasoline and naphtha samples containing only aromatics and saturated hydrocarbons were used.

A comparison of the data in columns 2 and 3 shows a reasonable agreement for most practical purposes. Owing to the solubility of saturated hydrocarbons in sulfuric acid, slightly higher values are obtained by the chemical method.

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Manganese and Chromium in Steel

Modified Persulfate-Arsenite Method

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THE persulfate-arsenite method for manganese is widely used in routine analysis of steel, since it is rapid, economical, and clean as compared with the alternative bismuthate method. In solutions as normally used, arsenite reduces septivalent manganese to more or less midway between the trivalent and quadrivalent state. Consequently the method suffers in reliability, since standardization is empirical and varies with the operator, and the end point is indefinite, particularly in the presence of sexivalent chromium.

Lang (*3*) found that the use of catalysts such as potassium iodide and iodate causes the reduction of permanganic acid by arsenite to proceed quantitatively to the bivalent condition in sulfuric or hydrochloric acid solutions. Bright (*1*) confirmed this and showed that arsenious oxide could be used as a direct primary standard in permanganimetry. Gleu (*2*) proposed the use of a 0.01 *M* solution of osmium tetroxide as catalyst, and Park (*4*) investigated and found satisfactory the use of this catalyst for evaluating manganese in steel by the bismuthate procedure, using arsenite as reducing agent.

In the present work it has been shown that osmium tetroxide is a suitable catalyst for the persulfate-arsenite method for manganese in steel. Potassium iodide and iodate were ineffective in the same solutions, because of precipitation by silver ions; but they were successful after precipitation of silver as chloride, provided excess hydrochloric acid was present in concentrations above 1 ml. of hydrochloric acid (1 to 2) per 150 ml. of solution. However, in the presence of these catalysts chromium is reduced from the sexivalent to the trivalent state. Chromium, if present, must be evaluated separately and manganese found by deduction.

Using the routine persulfate method on Ridsdale standard steels, arsenite with osmium tetroxide as catalyst gave high results for manganese. This was found to be due mainly to a direct oxidation of arsenite by undecomposed persulfate, and not to the reoxidation of manganese by persulfate. This direct oxidizing effect in equivalents of manganese was 0.17, 0.14, and 0.07 mg. for persulfate concentrations of 2.0, 1.0, and 0.20 gram per 150 ml., respectively. For accurate work by this method, almost complete decomposition of persulfate is necessary, and this means longer boiling periods. To stabilize permanganic acid throughout this period, the following reagent concentrations (per 100 ml. of solution) were found necessary and sufficient within the usual range of manganese concentrations:

Sulfuric acid (sp. gr. 1.84)	5 ml.
Phosphoric acid (sp. gr. 1.75)	2 ml.
Persulfate	2 grams
Silver nitrate	50 mg.

In such solutions the minimum period for effective decomposition of persulfate by boiling is 4 minutes. Permanganic acid is stable after an 8-minute boiling period. Chromium, when present, was satisfactorily determined on the same solution by the usual persulfate method. For the titration of sexivalent chromium arsenite was used with a 0.0025 *M* solution of potassium iodide as catalyst. Vanadium does not interfere and this is an advantage, since the permanganate end point is not subject to the fading that must be guarded against in the presence of vanadium, when ferrous sulfate is used for reduction. Owing to its stability, it is suggested that arsenite replace ferrous sulfate for volumetric determinations of chromium and manganese. The following tabulated results were obtained on Ridsdale steels "J" and "V", using the procedure described below; chromium was introduced where necessary by means of bichromate:

Standard Steel	Constituents Present			Constituents Found[a]		
	Mn	Cr	V	Mn	Cr	V
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
J	7.68	Nil	Nil	7.69	Nil	Nil
J	7.68	3.54	Nil	7.71	3.51	Nil
V	5.42	8.61	2.73	5.32	8.50	2.74

[a] Average of three determinations.

Manganese and Chromium on One Sample

SOLUTIONS REQUIRED. Silver nitrate, 10 grams dissolved in 1 liter of distilled water. Ammonium persulfate, 250 grams dissolved in water, filtered if necessary, and made up to 500 ml.

Sulfuric-phosphoric acid. Pour 1 liter of sulfuric acid into 6 liters of distilled water, and add 300 ml. of phosphoric acid (sp. gr. 1.75).

Sodium arsenite solution, 0.0316 *N*. Dissolve 7.8 grams of pure arsenious oxide in 500 ml. of distilled water and 50 ml. of sodium hydroxide (1 pound per liter). When completely in solution dilute to 5 liters with distilled water. Standardize against sodium oxalate through permanganate.

PROCEDURE. Transfer 1 gram of the steel drillings to a 500-ml. Erlenmeyer flask. Take up in 50 ml. of sulfuric-phosphoric acid mixture. Heat gently until in solution and then oxidize ferrous iron to ferric by adding 5 ml. of nitric acid (sp. gr. 1.20). Boil to expel oxides of nitrogen and add 50 ml. of distilled water and 5 ml. of silver nitrate solution.

Boil and add 5 ml. of ammonium persulfate solution. Boil for a further period of not less than 4 minutes and not greater than 6 minutes. Cool rapidly in a water bath to 25° C. Add 3 drops of osmium tetroxide (0.01 *M*) and then run in sodium arsenite in slight excess (5-ml. excess). Titrate excess arsenite by adding potassium permanganate dropwise to the first detectable pink tinge. The volume of arsenite so obtained represents manganese plus chromium (*a*).

Return solution to hot plate. Boil and add 5 ml. of persulfate solution. Boil the solution for 8 to 10 minutes, and run in 4 to 5 ml. of hydrochloric acid (1 to 3). Boil for 5 minutes after the pink color of the solution has been discharged. Cool to 25° C., add 3 drops of potassium iodate (0.0025 *M*), and run in a small excess of arsenite. Titrate to a faint pink tint with potassium permanganate. The volume of arsenite so used represents chromium (*b*).

By deducting (*b*) from (*a*) the manganese equivalent is obtained. For routine work the theoretical equivalent of arsenite and permanganate may be used for obtaining the permanganate equivalent of (*a*) and (*b*). However, for accurate work the volumes obtained for (*a*) and (*b*) must be corrected for dilution effect and color interference. This usually amounts to 0.2 to 0.3 ml. for chromium contents up to 1 per cent and should be added to both (*a*) and (*b*). This may be determined by boiling the solution after the final titration for 10 minutes. After cooling, the volume of potassium permanganate required to give a perceptible pink tint is noted and this volume added to both (*a*) and (*b*). Vanadium, if present, is best estimated on the solution remaining by the ferrous sulfate–persulfate method, followed by titration with potassium permanganate. In this the volume correction for dilution and color interference must be deducted from the potassium permanganate buret reading.

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Construction of Manometers for Measuring Flow

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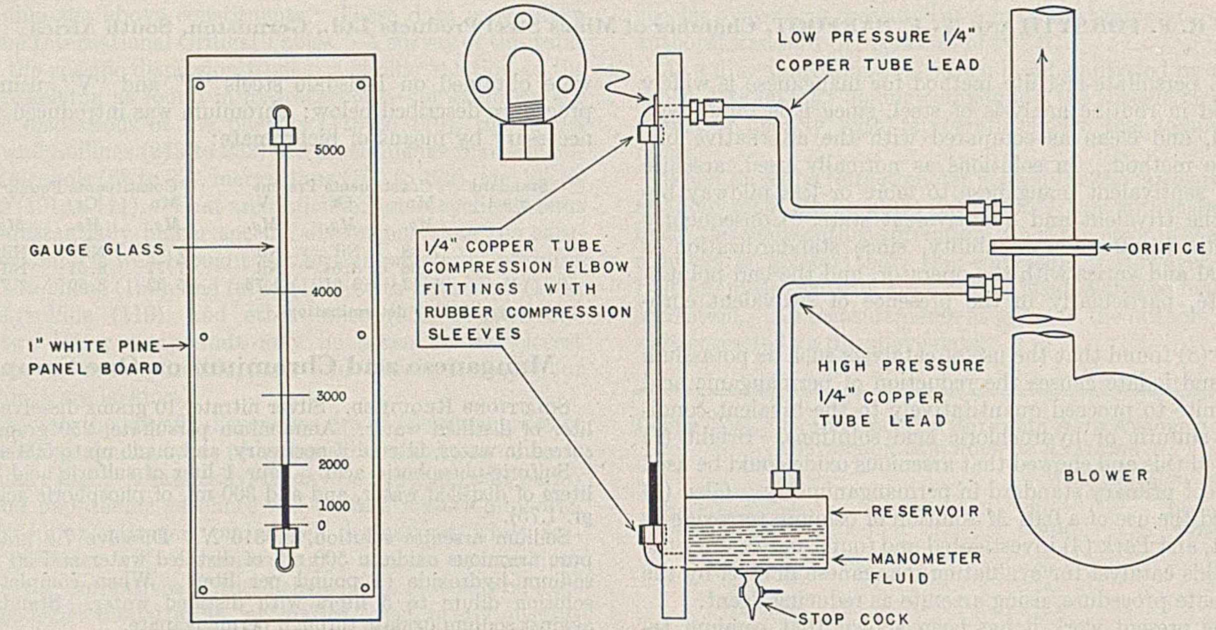

GAUGE GLASS
5000
4000
3000
2000
1000
0
1" WHITE PINE PANEL BOARD
1/4" COPPER TUBE COMPRESSION ELBOW FITTINGS WITH RUBBER COMPRESSION SLEEVES
LOW PRESSURE 1/4" COPPER TUBE LEAD
ORIFICE
HIGH PRESSURE 1/4" COPPER TUBE LEAD
BLOWER
RESERVOIR
MANOMETER FLUID
STOP COCK

FIGURE 1. DIRECT-READING FLOW MANOMETER GAGE

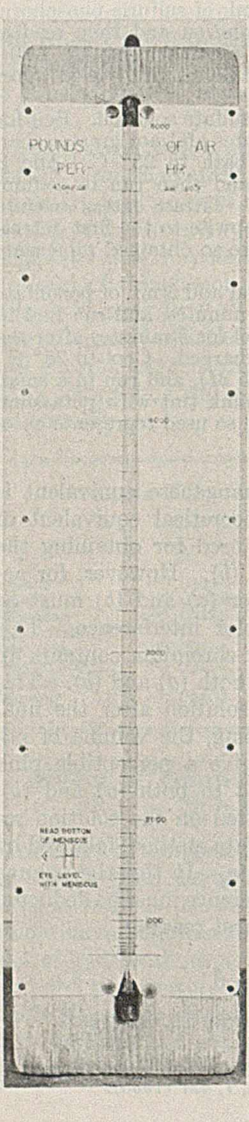

POUNDS OF AIR PER HR
READ BOTTOM OF MENISCUS
EYE LEVEL WITH MENISCUS

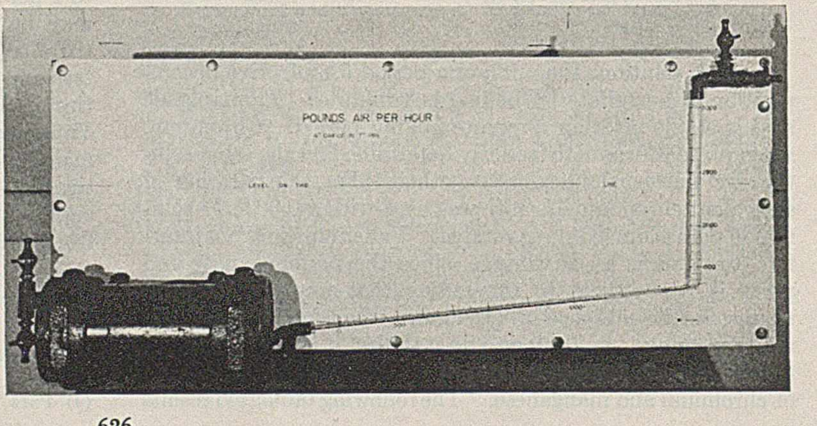
FIGURE 2 (*left*). DIRECT-READING FLOW MANOMETER GAGE

FLUID flow is frequently determined by measuring the pressure drop of the fluid across an orifice or Venturi. The equal-bore U-tube manometer is the simplest device for measuring this pressure drop, but the determination requires reading the two column heights and subtracting the lesser height from the greater. The pressure drop reading also requires conversion into flow units.

The several operations required to make a flow determination with an equal-bore U-tube are reduced to one operation with the direct-reading flow manometer gage shown in Figures 1 and 2. This instrument is built on the U-tube principle; however, one arm is a reservoir with a large horizontal cross section and the other arm is a small-bore glass tube. In all manometers, an external pressure difference across the instrument causes the liquid in one arm to be displaced into the other, so that the difference in column heights creates a pressure equal and opposite to the external pressure. If the greater external pressure is connected to the reservoir of the manometer shown in Figure 1 and the smaller pressure to the tube, a very slight depression of the manometer liquid in the reservoir forces the liquid in the tube to the equilibrium level. In the particular instrument shown, a 0.04-cm. (0.016-inch) depression of the reservoir level causes a 75-cm. (30-inch, full-scale) rise in the tube. For practical purposes, the rise in the tube column can be considered the pressure difference reading and the flow scale plotted directly behind the tube for a given fluid density. The correction for the change in the reservoir level is a lineal function of the tube column height (assuming the cross section of the tube and reservoir constant) and is dependent upon the ratio of tube and reservoir cross-section areas.

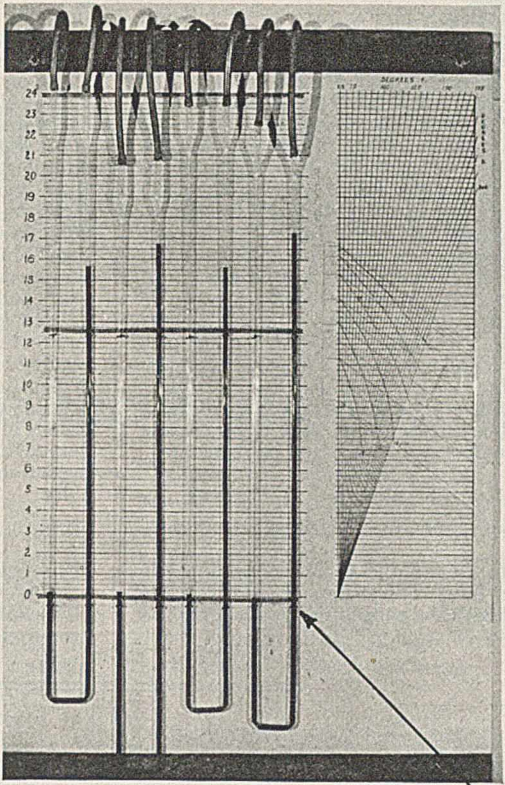
The gage shown in Figure 1 is constructed of simple materials at very moderate cost. The reservoir consists of 0.3-cm. (0.125-inch) steel plate welded together into a box with the plate facing

FIGURE 3. DIRECT-READING MANOMETER GAGE WITH INCLINED SCALE


POUNDS AIR PER HOUR

the gage panel extending beyond the box to accommodate the bolts that hold it to the panel board. A 0.3-cm. petcock is brazed into a hole in the bottom of the reservoir for filling and draining. A 0.6-cm. (0.25-inch) copper tubing compression elbow is brazed into a hole in the side facing the panel board, so as to project through a hole in the panel board and receive the end of the glass tube. A 0.6-cm. copper tubing compression fitting is also brazed into a hole in the top of the reservoir to receive the high-pressure lead.

The small-bore glass tube is ordinary laboratory tubing, about 6 mm. in outside diameter, and fits nicely into 0.6-cm. copper tubing compression fittings. The compression rings in the copper tubing fittings are replaced with rings cut from rubber tubing 6 mm. in inside diameter. The top of the glass tubing is received by another 0.6-cm. copper tubing compression elbow. A bracket is brazed to this elbow and holds the fitting in a hole in the panel board. The panel board is of shellacked white pine 2.5 cm. (1 inch) thick, 20 cm. (8 inches) wide, and 90 cm. (36 inches) long, cut out for the copper tubing elbows and drilled for the reservoir bolts. The scale is computed from orifice formulas (*1*) and plotted on tracing paper. Prints of the scale are mounted on the panel board behind the glass tube, so that the zero point is level with the midpoint of the reservoir. The manometer liquid is brought to the zero point when the gage is properly leveled.



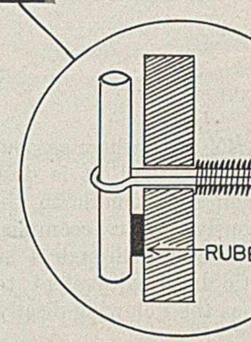


FIGURE 5. U-TUBES FOR MEASURING PERFORMANCE OF FOUR FANS OPERATING IN PARALLEL

The choice of a manometer liquid is important. When water is used as the manometer liquid in the gage shown in Figure 1, which is used to measure air flow, momentary flow fluctuations make readings difficult. A light mineral oil has sufficient viscosity to damp out these fluctuations, and, unlike water, does not freeze or evaporate. A constriction in the line will also cause dampening, but is subject to clogging from dirt. A trace of red dye added to the oil greatly facilitates gage readings.

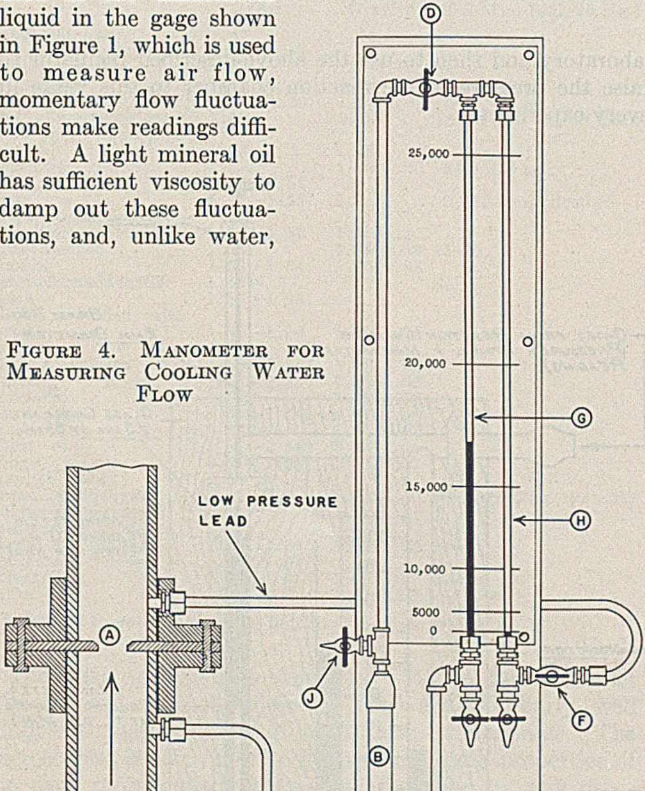


FIGURE 4. MANOMETER FOR MEASURING COOLING WATER FLOW

Because the flow scale is a function of the square root of the pressure drop, the high-flow portion of the scale of a vertical tube is more sensitive to variations than the low portion. The gage shown in Figure 3 overcomes this objection by having the low portion of the scale rise on a slope and the high portion rise vertically. A tube, bent in the shape of the curve of the following equation, will have equally spaced divisions for equal increments of flow throughout the entire range.

$$x = \sqrt{\frac{y}{4k} - y^2} + \frac{1}{4k} \sin^{-1} (2 \sqrt{ky})$$

x and y are abscissa and ordinate, respectively. The constant, k, in this equation must be chosen so that the maximum value, y, is less than $\frac{1}{4k}$, as the curve becomes imaginary when y is greater than $\frac{1}{4k}$.

The manometer shown in Figure 4 was designed to measure the flow of water through an orifice and has the novel feature that the same water is used as the manometer liquid. This gage is essentially an inverted equal-bore U-tube with a pump to regulate the air pressure above the manometer water columns and thus adjust the lower level column to a scale zero point. The air pump is also operated by the water whose flow is being determined.

The operation of the gage shown in Figure 4 is as follows: From the orifice, *A*, the high-pressure lead is connected to the manometer arm, *G*, through valve *E* and to the air pump, *B*, through valve *C*. Valve *C* is opened and admits water to the pump and compresses the air in the top of the pump and U-tube. *C* is then closed and valves *E* and *F* are opened, admitting water from the high- and low-pressure orifice leads to manometer arms *G* and *H*, respectively. The level of the water in the low-pressure tube, *H*, will not rise to the zero point because the level of the pump, *B*, gives greater air pressure in the manometer than is necessary. Leaving valves *E* and *F* open, valve *I* is opened slightly, relieving some of the water trapped in pump *B* and thus the air pressure in the manometer arms, and letting the water level in the manometer tubes rise. When the water level in *H* reaches the zero point, *I* is closed and the height of the water in *G* read directly on the flow scale. Valves *D*, *I*, and *J* and the petcocks at the bottom of the manometer tubes are used to empty water from the pump and tubes.

This gage is readily made from standard pipe and copper tubing fittings. Heavy-walled rubber tubing leads and a removable orifice piping section make temporary installation convenient.

Figure 5 shows a quickly assembled set of U-tubes for measuring the performance of four fans operating in parallel.

Each U-tube is connected to the fan ducts so as to measure the static pressure across each fan. The tubes themselves are mounted on a flexboard panel with the wire slip rings shown in the insert of Figure 5, which allows them to slip up and down like a trombone slide. In this way, the lower liquid column of each U-tube is set on the zero line of the scale behind the tubes. Rubber strips on the scale prevent the tubes from slipping.

The high liquid column is read directly on the scale which is calibrated in inches. To the right of the inch scale is a scale of cubic feet per minute delivered by the fan at standard conditions and plotted from the manufacturer's tables of fan performance at the r. p. m. used. The triangle to the immediate right of the cubic feet per minute scale is a chart which converts the reading to cubic feet per minute delivered at the temperature of the air passing through the fan or at standard conditions but corrected for the temperature of the air passing through the fan. (Laying out this chart follows directly from Charles' law. The isothermal lines are straight lines radiating from the origin with equal increments subtending equal angles.) Horizontal projection of the U-tube reading through the chart (which can be done visually) gives any of the delivery figures described above. Many fans have two possible deliveries at the same static pressure; however, only one occurs in the normal operating range, the other occurring when very little air is passing through the fan. Any static pressure measurement of fan performance would be subject to this difficulty.

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Pressure Regulator for Dynamic Gaseous Systems

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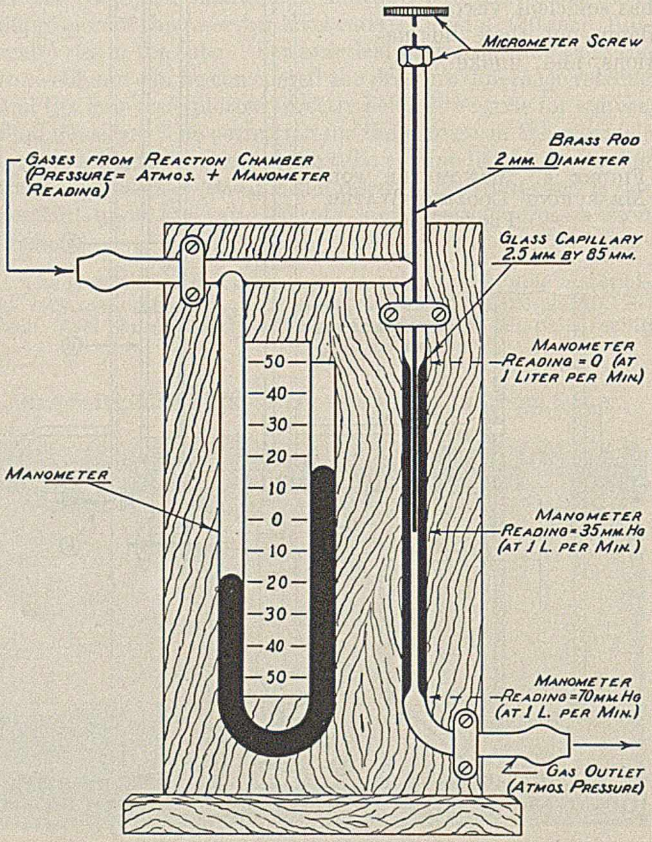
Sun Oil Company Experimental Division, Norwood, Penna.

IN MANY cases where gaseous reactions are studied by the dynamic method, it is desirable to maintain pressures higher than atmospheric in the reaction chamber. While this obviously can be accomplished by bubbling the gaseous reaction products through a suitable liquid seal having a hydrostatic head equivalent to the desired pressure, this method has the following disadvantages:

1. Continuous fluctuation in pressure will occur, owing to the bubbling through the liquid.
2. The gaseous reaction products will be contaminated with the liquid through which the gas is bubbled.
3. Certain constituents of the reaction products may react with or dissolve and condense into the liquid to a greater extent than other compounds.

In order to avoid these disadvantages, a new pressure regulator has been developed. As shown in the figure, it is very simple in design and consists essentially only of a glass capillary tube 2.5 mm. in diameter and 85 mm. long and a brass rod (platinum or glass for reaction products containing corrosive gases) which is 2 mm. in diameter. By means of a micrometer screw (or a rubber stopper) the wire may be inserted to any desired extent into the glass capillary, thus increasing the frictional resistance which controls the pressure in the reaction chamber or the system.

In addition to being used for maintaining various pressures in the gaseous reaction chambers, the new device may be used in the calibration of flowmeters which are to be used at pressures higher than atmospheric, or for accurate calibrations on days when the atmospheric pressure is below normal. Another application is expected to be found by investigators of gaseous reactions desiring to maintain a constant pressure throughout the series of experiments regardless of variation in atmospheric pressure. In such cases, it is believed that it will be advisable to select a pressure corresponding to the highest atmospheric pressure expected at the location of the laboratory and then to use the above-described regulator to raise the pressure in the reaction chamber to this value in every experiment.


MICROMETER SCREW
BRASS ROD 2 MM. DIAMETER
GASES FROM REACTION CHAMBER (PRESSURE= ATMOS. + MANOMETER READING)
GLASS CAPILLARY 2.5 MM. BY 85 MM.
MANOMETER READING = 0 (AT 1 LITER PER MIN.)
MANOMETER
MANOMETER READING = 35 MM. HG (AT 1 L. PER MIN.)
MANOMETER READING = 70 MM. HG (AT 1 L. PER MIN.)
GAS OUTLET (ATMOS. PRESSURE)
50
40
30
20
10
0
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40
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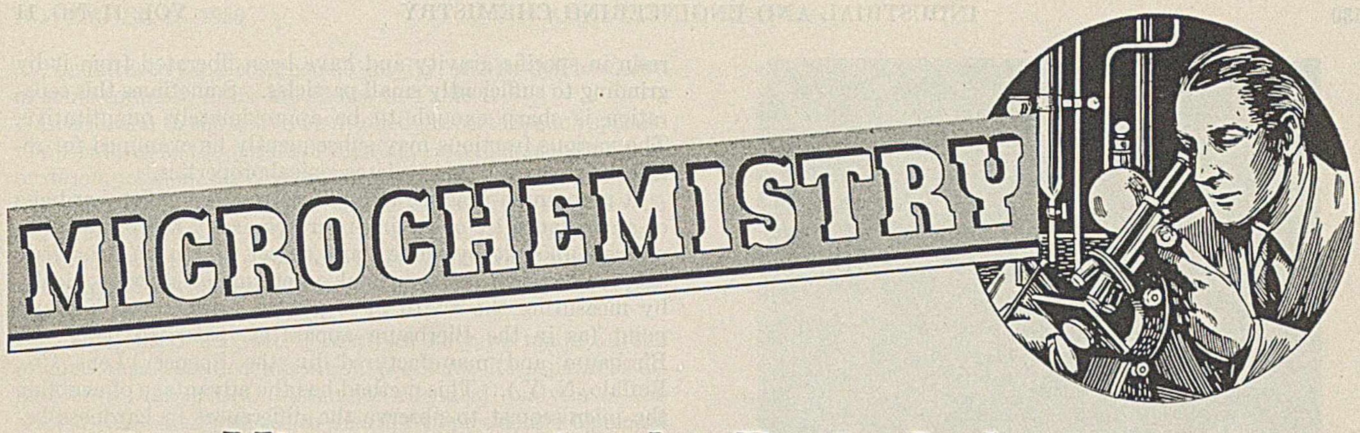

Microscopy in the Resin Industry

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TO A microscopist, the investigation of resins and their plastics is an interesting and important field because it gives him boundless opportunity to exercise his technique and his ingenuity. There are so many different natural and synthetic resins (*5*), each capable of assuming fluid, plastic, or elastic forms, that almost every case requires a fresh attack. Moreover, a great variety of other materials, with microscopical characteristics and optical properties, are often used as fillers or components; their distribution and identification are also important matters.

TABLE I. PROPERTIES OF RESINS[a]

	Refractive Index	Specific Gravity	Brinell Hardness (2.5-Mm. Ball, 25 Kg.)
Ethyl cellulose	1.47	1.14	
Cellulose acetobutyrate	1.47		
Cellulose acetate (molded)	1.47 –1.50	1.27–1.63	7 (10 kg.)
Cellulose acetate (sheet)	1.49 –1.50	1.27–1.37	6–11 (10 kg.)
Methyl methacrylate	1.49	1.18	18–20 (500 kg., 10 mm.)
Ester gum (rosin-glycerol)	1.49 ±	1.08–1.09	
Acrylates	1.5	1.35–1.60	8–11 (10 kg.)
Cellulose nitrate	1.50 –1.51		
Glass	1.47 –1.55	2.2	0.015 (mm. deep.)
Alkyd resins (glycerol-phthalic anhydride)	1.51 –1.57	1.1 –1.3	
Vinyl acetate	1.53	1.34–1.36	15–25
Manila	1.53 –1.54	1.06–1.08	
Casein-formaldehyde	1.54 ±		23
Rosin	1.53 –1.55		
Alkyd, modified with rosin	1.54 –1.56	1.11–1.14	
Shellac	1.53		
East India resins	1.538–1.543	1.00–1.06	
Damar	1.535–1.536	1.04–1.06	
Pontianak	1.540	1.07–1.08	
Boe Manila	1.539–1.540	1.07–1.08	
Sandarac	1.545	1.05–1.09	
Kauri	1.544–1.546	1.03–1.05	
Congo	1.540–1.541	1.05–1.07	
Vinyl chloride	1.54		
Urea-formaldehyde	1.54 –1.6	1.48–1.50	48–54 (500 kg., 10 mm.)
Rubber (chlorinated)	1.56	1.5	
Sulfonamide-aldehyde	1.59		
Phenol-formaldehyde	1.58 –1.65	1.27–1.32	30–45
Coumarone-indene	1.62 –1.64		
Polystyrene	1.60 –1.67	1.05–1.07	20–30
Sulfur	1.9 –2.3	1.92–2.07	

[a] Some of these data are to be found in (*2*; *3*, p. 384; *4*).

The resin technologist welcomes a wider application of microscopical methods because they are peculiarly well adapted to the examination of his complex materials. The microscopist is often able to determine certain properties of the resin more quickly than could be done by any other method. Just as often, his methods offer the only means of determining these properties. When necessary, the adapted methods of the biologist, petrographer, colloid chemist, mineralographer, and physical tester may all be pressed into service.

In this paper, the word "resin" is taken in a broad sense to mean any essentially amorphous material which may be rendered plastic under specified conditions of temperature and pressure. The paper is concerned with the application of micromethods, especially microscopical ones, in the study of typical resins for various commercial uses. The few illustrations given below have been chosen as typical examples of the many microscopical problems which are being investigated in the industrial research on resins.

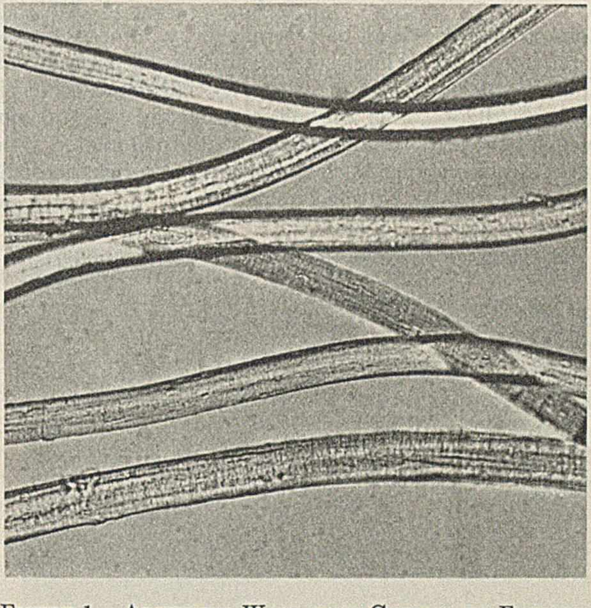

FIGURE 1. ARTIFICIAL WOOL FROM CASEIN AND FORMALDEHYDE (× 200)

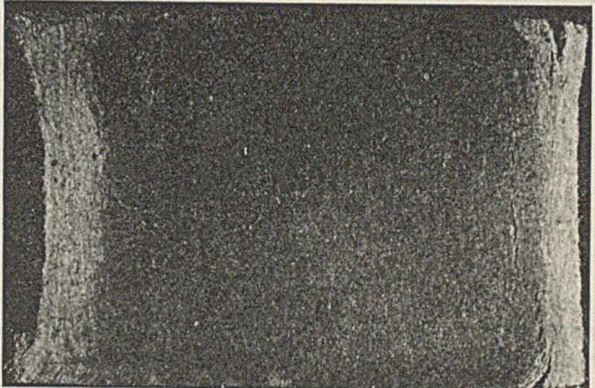

FIGURE 2. CROSS SECTION OF LAMINATED PAPER, IMPREGNATED ON BOTH SIDES WITH SULFUR (× 3)

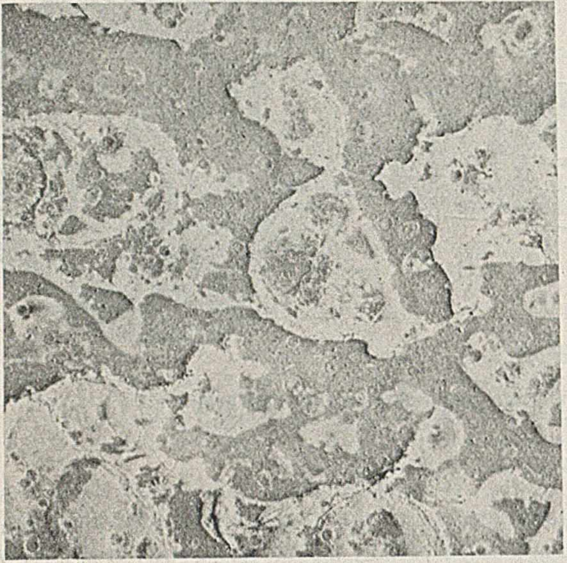

Figure 3. Erosion Spots on an Enamel after Accelerated Weathering in Weatherometer (× 15)

Physical Properties

Refractive indices may be determined by immersion methods, provided that at least some microscopical particles may be found sufficiently free of other physical phases, like pigments and fillers. This method is much quicker and more convenient than a determination on the refractometer, which requires a relatively large, clear piece with two perpendicular surfaces, one of them polished.

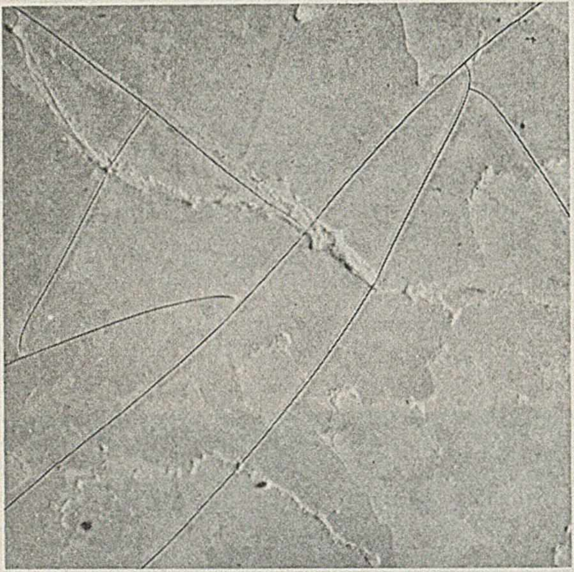

Figure 4. Microscopic Cracks and Erosion Spots on Brittle Enamel after Accelerated Weathering in Weatherometer (× 15)

Specific gravity may be determined in a micro way by immersing some of the finely powdered resin in liquids of standardized specific gravity and noticing whether the particles sink or float. This procedure frequently serves also to separate out fillers and other materials which differ from the resin in specific gravity and have been liberated from it by grinding to sufficiently small particles. Sometimes this separation is sharp enough to be approximately quantitative. The various fractions may subsequently be examined for refractive index and other microscopical properties.

It is common practice to measure the impression hardness of a substance by observing microscopically the pattern impressed upon it by some hard object of known geometric shape. Scratch hardness is also determined microscopically by measuring the width of a scratch made by a diamond point (as in the Bierbaum apparatus, patented by C. H. Bierbaum and manufactured by the Spencer Lens Co., Buffalo, N. Y.). This method has the advantage of enabling the microscopist to observe the differences in hardness between microscopical areas of different constituents in the same resin.

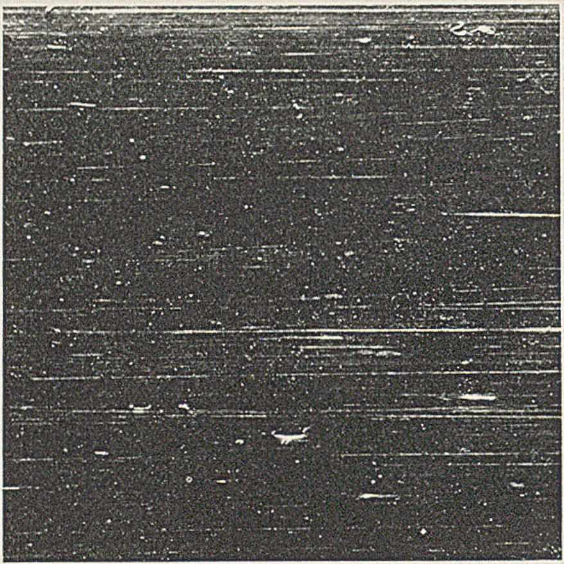

Figure 5. Rubber Tire Stock (× 5)

Stretched twice its length, orthogonal light. Normal behavior of accelerator

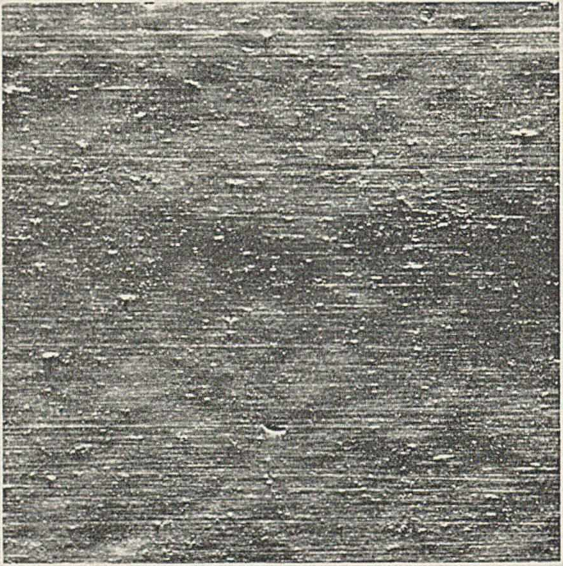

Figure 6. Rubber Tire Stock (× 5)

Stretched twice its length, orthogonal light. Localized, overactive accelerator

The refractive indices, specific gravity, and Brinell hardness of some common resins are shown in Table I.

In addition to the above-mentioned properties, such specific temperatures as the points of melting, softening, sublimation, or decomposition, may be determined on the hot stage of the microscope. Solubility in determinative solvents may also be observed. The microscope has proved to be a valuable accessory lately in such physical tests as electrical breakdown potential, ultraviolet radiation effects, temperatures of scorching, and variations in humidity.

Microscopical qualitative analyses may be made on the original resin, its decomposition products, its separable fillers, or its impurities. A similar chemical analysis of the ignited ash usually serves to identify the inorganic pigments and the inorganic bases of organic lakes.

Petrographic analyses serve to identify fragments of minerals and synthetic chemicals in natural resins. Microscopical characteristics indicate the presence of portions of insects and vegetable fibers in such resins.

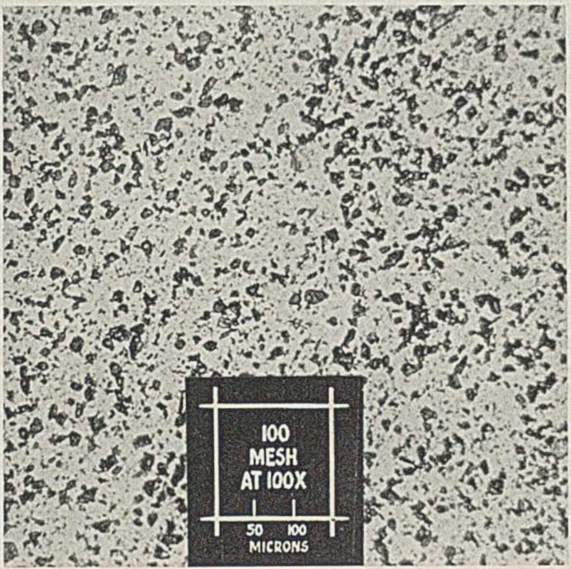

FIGURE 7. COMMERCIAL GROUND RUBBER SULFUR (× 100)

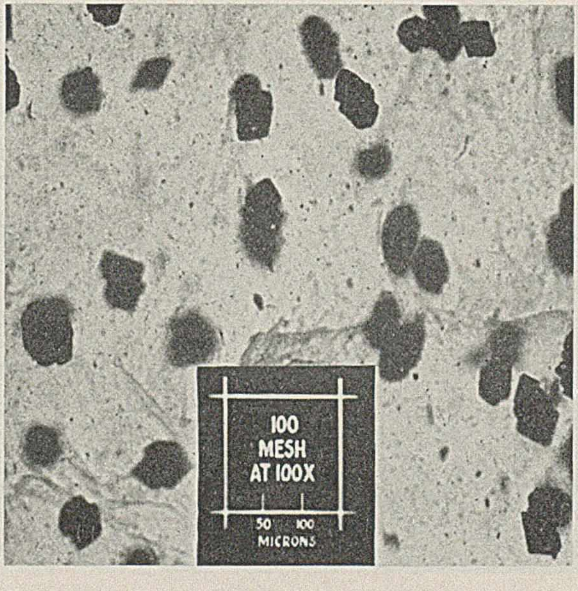

FIGURE 8. THIN SECTION OF MILLED UNVULCANIZED RUBBER, CONTAINING 3 PER CENT OF SULFUR (× 100)

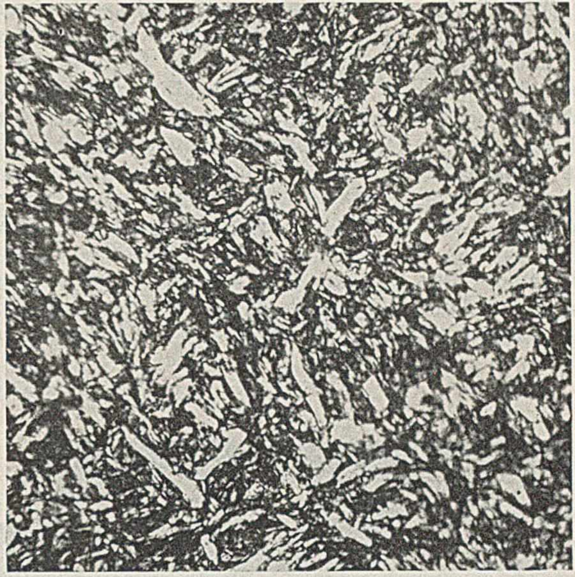

FIGURE 9. THIN SECTION OF UREA-FORMALDEHYDE RESIN BETWEEN CROSSED NICOLS (× 100)

Microscopical Characteristics of Resin

The amorphous nature of a resin is characteristic, but occasionally, under certain conditions, a crystalline phase makes its appearance.

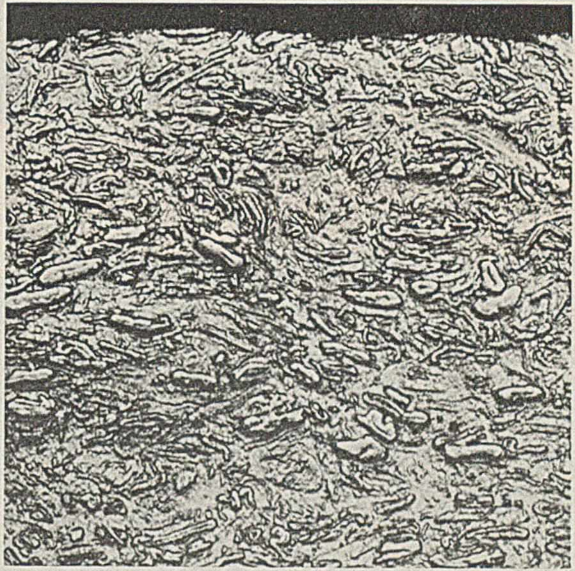

FIGURE 10. UREA RESIN WITH PAPER PULP FILLER (× 250)

Polished cross section, showing normal distribution of fibers

The examination of resins under the microscope is also useful for the explanation of turbidity and opacity, in spots or throughout the resin. These phenomena are usually caused by tiny gas bubbles, pigment particles, impurities, microscopic crystals, nonplastic resin, or decomposition products.

The microscope is also a handy tool in the study of textile and brush fibers made from synthetic or semisynthetic resins like the cellulose esters, regenerated cellulose, casein-formaldehyde, other coagulated proteins, vinyl resins, and glass. The microscopical examination of these fibers is not only extremely important in their identification, but also in the explanation of certain special properties such as delustering, curl, and crimp. Figure 1 shows the microscopical appearance of an artificial wool. By its original appearance, its behavior in reagents under the microscope, and a few organic qualitative analyses, it was identified 5 years ago as casein-formaldehyde.

Resins are also used as adhesives, binders, and stiffening agents, as in laminating wood, cloth, and paper, and making sheets of ground cork. Figure 2 shows a cross section of laminated paper, re-enforced on both sides (edges) with sulfur, a good, but relatively uncommon, resin.

The use of resins as surface coatings is a very extensive field in itself. They are used in paints, varnishes, lacquers, and printing inks, and as finishes for both papers and fabrics. The microscopical work includes the examination of the resin surface before and after it has undergone various empirical and practical tests. Space does not permit a more thorough discussion of this important field, but it is interesting to note the microscopical appearance of the erosion spots on a test panel after exposure in the Weatherometer, as shown in Figure 3. Microscopic cracks which developed, upon exposure in the Weatherometer, on a very brittle enamel film are shown in Figure 4.

The stresses and strains in brushed, dipped, and sprayed

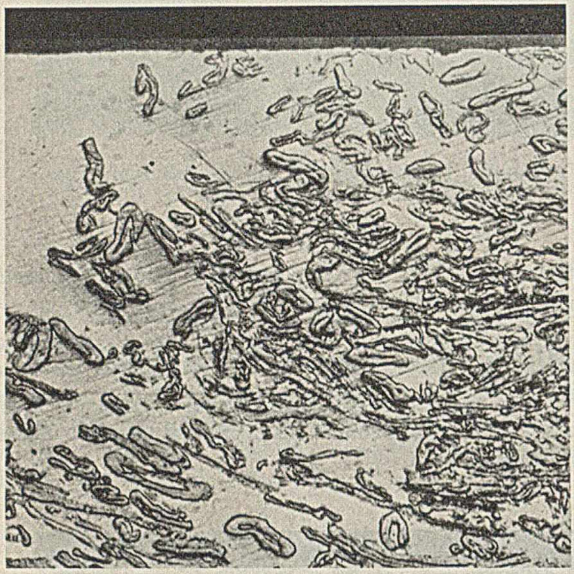

FIGURE 11. PHENOLIC RESIN WITH PAPER PULP FILLER (× 250)

Polished cross section, showing extreme segregation of fibers

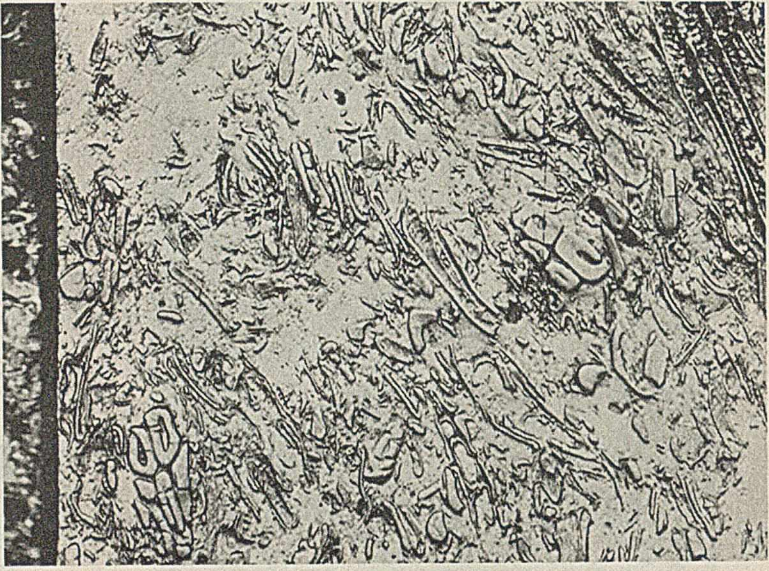

FIGURE 13. PHENOLIC RESIN WITH WOOD FLOUR AS FILLER, POLISHED CROSS SECTION (× 250)

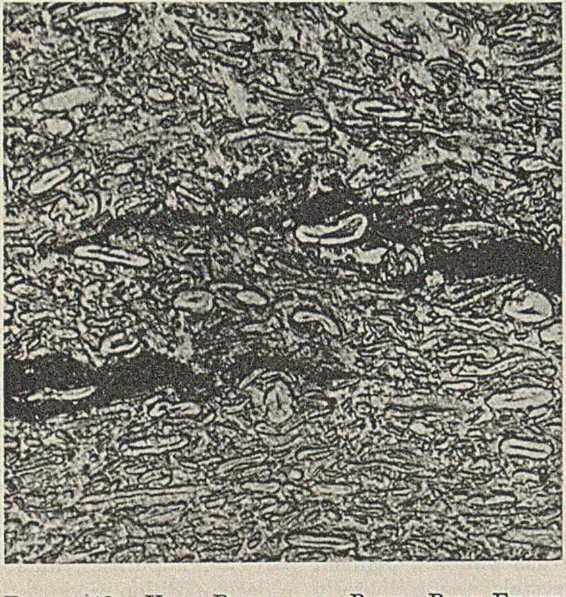

FIGURE 12. UREA RESIN WITH PAPER PULP FILLER (× 250)

Polished cross section, illustrating effect of heat on molded piece

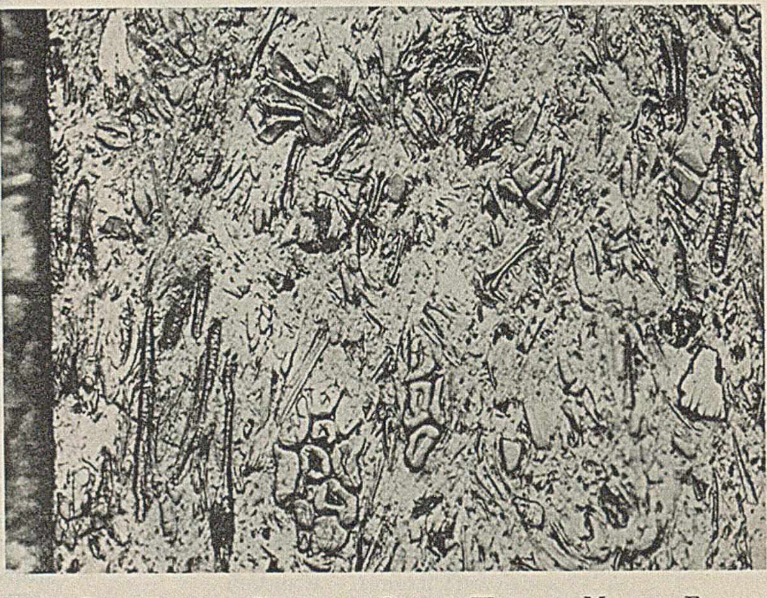

FIGURE 14. PHENOLIC RESIN WITH GROUND WOOD AND MINERAL FILLERS POLISHED CROSS SECTION (× 250)

films and cast and molded forms are all distinguishable with polarized light, especially under the microscope.

An article by Weigel (*6*) came to hand after the preparation of this manuscript. It is heartily recommended to the microscopical investigator of synthetic molded resins. The author relies chiefly on stains to differentiate fillers from the resin.

The surface of a fabricated resin may often indicate phenomena which have taken place within it. Figure 5 shows the surface of a piece of rubber tire stock with a normal appearance after stretching to twice its original length (*1*). Figure 6 shows another sample pictured under identical conditions but containing segregated particles of an accelerator whose action was so rapid that it cured certain small areas of the rubber below the curing temperatures, with the result that, after curing, these areas were not so elastic as their matrix, and they appeared as tiny bumps when the piece was stretched.

Internal Structure of Molded Resins

THIN SECTIONS. Sometimes the internal structure of a resin may be shown microscopically in transmitted light by cutting a cross section sufficiently thin. For comparison with the next photomicrograph, Figure 7 shows a sample of commercial, ground rubber sulfur, as received. Figure 8, under the same magnification, shows a microtomed section of milled rubber, before vulcanization, containing 3 per cent of the same sulfur. This photomicrograph shows that a few of the sulfur particles have grown into large crystals or clusters of crystals, with free rhombic faces, at the expense of other particles.

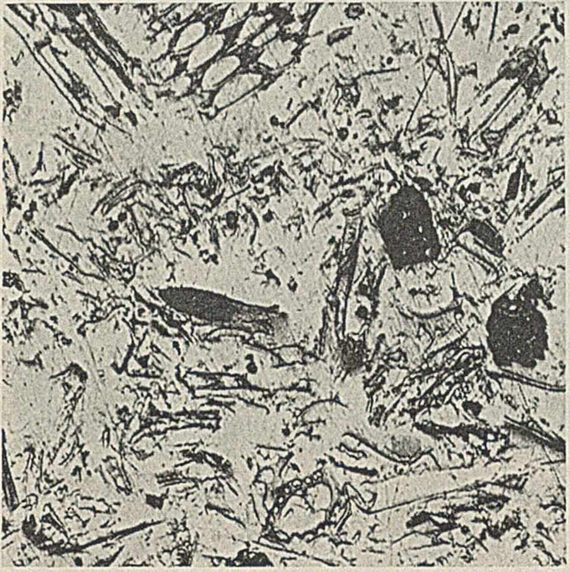

FIGURE 15. HEMP HURDS IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION (× 250)

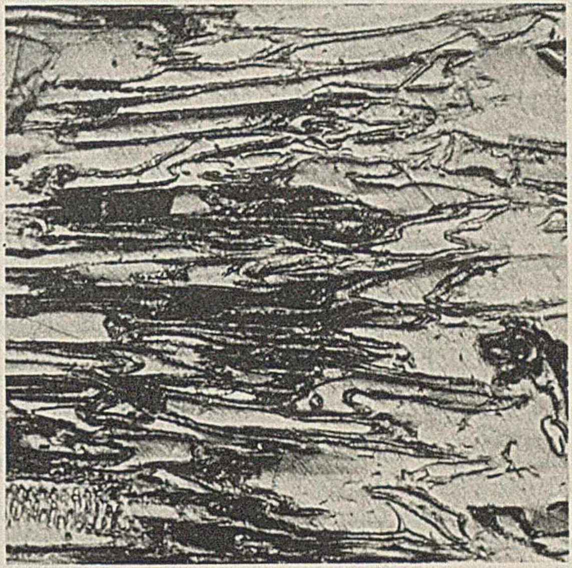

FIGURE 17. SUGAR CANE IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION (× 250)

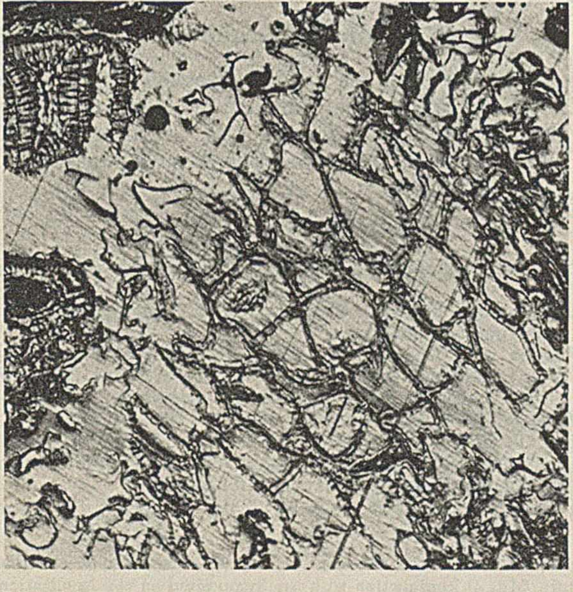

FIGURE 16. CORK IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION (× 250)

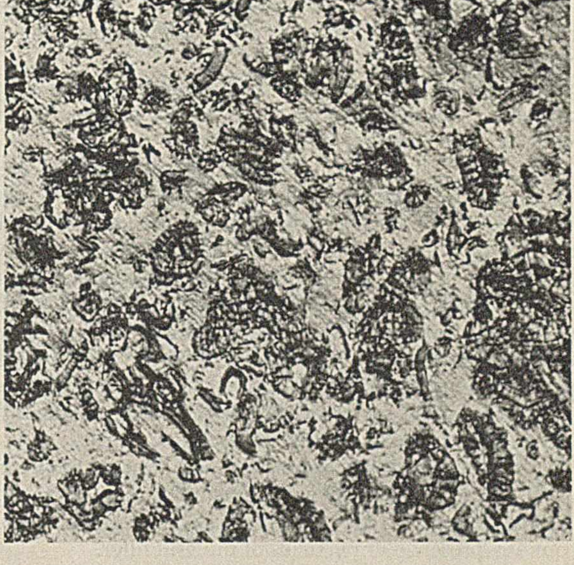

FIGURE 18. WALNUT SHELLS IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION (× 250)

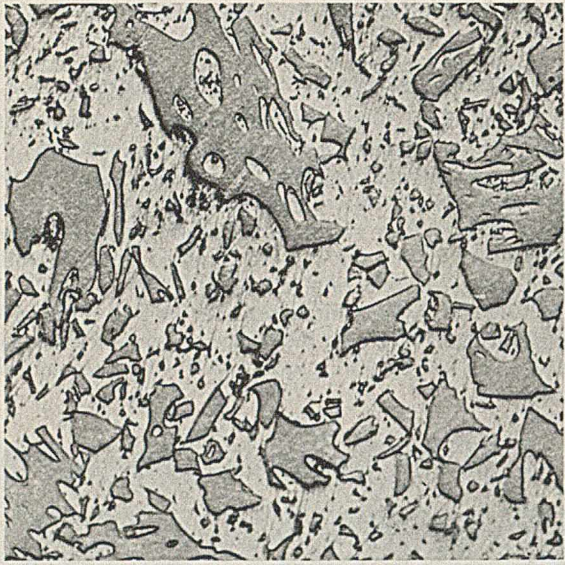

Figure 19. Pumice in Molded Phenolic Resin, Polished Cross Section (× 250)

Sometimes a thin section may be ground mechanically from a molded resin. Figure 9 shows a ground thin section of a urea-formaldehyde resin, between crossed Nicols, to show the fibers of alpha-cellulose pulp. Recently, the author has found that the shaving removed from a urea-formaldehyde molding, by turning it on a lathe, is very satisfactory for microscopical examination. A shaving of ample length can easily be made with a uniform thickness of 0.025 mm. (0.001 inch, or 25 μ).

Polished Cross Section. The examination of opaque molded resins is usually done more quickly and easily in polished cross section than in thin section. (Details for preparing and examining polished cross sections of molded and laminated resins are to be published later.) In addition, a polished section is easier to prepare in a specially oriented section, such as a cross section through the molded surface.

Figure 10 illustrates the microscopical appearance of a cross section of a molded urea-formaldehyde resin containing chemically prepared paper pulp. The section is perpendicular to the molded surface, and the upper edge of the section represents the molded edge. Notice the shortness of the discrete paper fibers and the uniformity of their distribution, even out to the molded edge.

Figure 11 shows an example of extreme segregation of the paper fibers. The molded edge of the fiber-free area lies in a spotted area on the molded surface.

The area shown in Figure 12 is a portion of a molded piece of urea resin which had been used in measuring the elevated temperatures at which the resin became opaque and finally brown. Notice that the resin has darkened in places and that cracks originate in these areas and continue between the fibers.

Other Vegetable Fillers. The distribution of the fibers of ground wood in molded resin is illustrated in Figures 13 and 14. Figure 13 shows that some of the fiber bundles are relatively large. They are shown in longitudinal, diagonal, and transverse sections. Near the molded edge, the fibers are relatively small and, in some places, scarce.

In Figure 14, the fibers are smaller and much more uniformly distributed. The fibers are usually oriented parallel to the molded edge. The photomicrograph also serves to point out the presence of particles of mineral filler.

The next four photomicrographs show the microscopical appearance in polished cross section of molded resin containing some less common fibers which might be encountered in analytical work. Figures 15 through 18 are photomicrographs, respectively, of hemp "hurds" (hemp pith), cork, sugar cane, and walnut shells, each molded in a phenolic resin.

Mineral Fillers. Some mineral fillers may be identified by their microscopical structure by means of light vertically reflected from a polished cross section, even though the minerals are usually classified as transparent (poor reflectors).

Figure 19 illustrates the peripheral and internal structure of cross sections of pumice particles. The presence of internal voids and the curved indentations in the outline of the fragments would serve to identify the filler quickly.

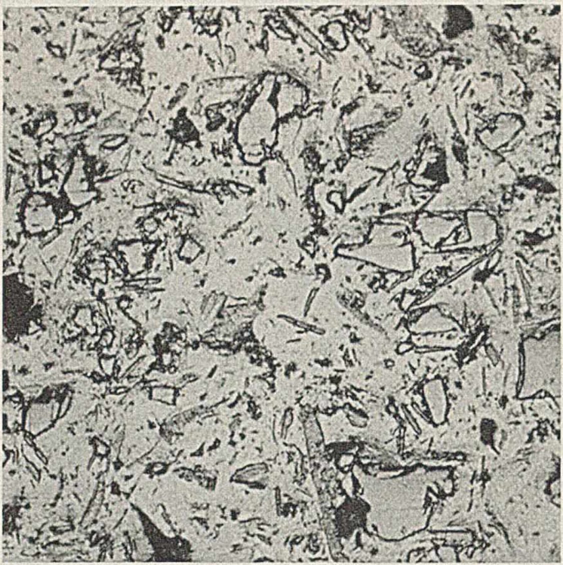

Figure 20. Talc in Molded Phenolic Resin, Polished Cross Section (× 250)

In Figure 20, some of the particles appear fragmental but others are thin and elongated (almost fibrous). These latter may be edge views of flaky particles or they may be actually fibrous. The elongated views are characteristic of certain varieties of talc minerals.

Acknowledgment

The author is indebted to his colleagues, R. L. Gilbert, R. W. Stafford, and L. Boor, for their aid in the collection of these data, and to C. W. Mason and E. G. Rochow for their very helpful advice in the preparation of the manuscript.

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(6) Weigel, W., *Kunststoffe*, 28, 5–8 (1938).

Presented at the 97th Meeting of the American Chemical Society, Baltimore, Md., in conjunction with the Symposium on the Application of Micro- and Semimicromethods to Industry, held jointly by the Divisions of Microchemistry and Industrial and Engineering Chemistry.

A Semimicro-Kjeldahl Distillation Apparatus

C. E. REDEMANN, California Institute of Technology, Pasadena, Calif.

NUMEROUS designs have been published for both macro- and micro-Kjeldahl distillation units. Some of these are very satisfactory in their performance, but all show some tendency to suck back the standard acid unless considerable care is exercised by the operator. A few require for fabrication a degree of skill in glass blowing seldom attained by anyone other than a professional glassblower. Various sources of error in both the macro- and micro-Kjeldahl determination of nitrogen have been discussed by Schulek and Vastagh (*2*). The use of rubber connections, to which these authors strongly object, is less objectionable than was formerly the case because of the high grade of amber-colored pure gum tubing and stoppers now available, and the small area of rubber in contact with the steam which suitable design readily reduces to less than 1 sq. cm. The loss in ammonia resulting from the large volume of air diluting the ammonia in the early part of the usual Kjeldahl distillation, to which Miller (*1*) has called attention, is best prevented by sweeping out the air in the apparatus with steam before liberating the ammonia with alkali.

The semimicro-Kjeldahl distillation unit herein described possesses the following advantages: Distillation is carried out from the same flask in which the digestion is performed, which in this case is a standard 100-ml. Pyrex Kjeldahl distillation flask. No ammonia is liberated until all the air has been swept out of the apparatus with steam. None of the standard acid in the receiver is sucked back into the distillation flask. The entire apparatus may be assembled on a single small-sized ring stand, thus making the unit both rigid and easily portable. A large number of determinations can be made with a single piece of apparatus in a short time, since cleaning is extremely rapid and distillation of the ammonia requires only a few minutes. In addition, the apparatus is built in three closely coupled units, any one of which may be easily removed for repair in the event of breakage.

Construction

The construction of the apparatus is adequately explained by Figure 1.

The capillary tip below the stopcock should have a bore between 2 and 3 mm. If the bore is smaller than 2 mm. the sodium hydroxide runs in too slowly, while if the bore is much larger than 3 mm. a solid column of liquid fails to form and steam may be expelled through the funnel top above the stopcock. The inner tube in the condenser must be of thin-walled glass to give adequate heat transfer.

The small trap on the filler tube in the steam-generating flask prevents water from spurting out of it during distillation, at the same time leaving the flask open to atmospheric pressure. As a consequence, if the standard acid starts to suck back out of the receiver, it rises only a few centimeters in the delivery tube before a few bubbles of air are drawn through the filler tube into the apparatus. These bubbles having restored atmospheric pressure within the apparatus, the distillation then continues without interruption. Water may also be run into the flask without removing the filler tube from the apparatus. The tube below the small trap in the filler tube should be at least 25 cm. in length and should extend nearly to the bottom of the large flask. The style of trap used here has been found very efficient and is desirably compact.

Operation

A 20- to 60-mg. sample is weighed into a 100-ml. Pyrex Kjeldahl distilling flask, and 2 to 5 ml. of C. P. concentrated sulfuric acid and any one of the numerous catalysts that have been suggested are added, the selenium-mercury-potassium sulfate mixture (*3*) being one of the best. Digestion is then completed in the usual manner. The flask and contents are allowed to cool to room temperature, after which 15 to 20 ml. of distilled water are added and the contents of the flask are well mixed. During the digestion of the sample the large flask in the distillation unit is filled approximately two-thirds full of distilled water and heated to boiling with an efficient burner. A blank Kjeldahl flask is fitted in place and the apparatus is well steamed. The blank Kjeldahl flask is now removed and replaced by one containing the diluted digested sample. A second burner is placed under the Kjeldahl flask and the two burners are so regulated that a moderate current of steam passes into the Kjeldahl flask. In the meantime a 200-ml. conical flask containing an appropriate amount of standard acid is placed under the delivery tube with the tip of the delivery tube about 1 cm. below the surface of the acid.

After the apparatus is completely filled with steam, the burner is temporarily removed from under the Kjeldahl flask and 10 to 15 ml. of 18 N sodium hydroxide solution, which has been allowed to stand until carbonate-free, are added in

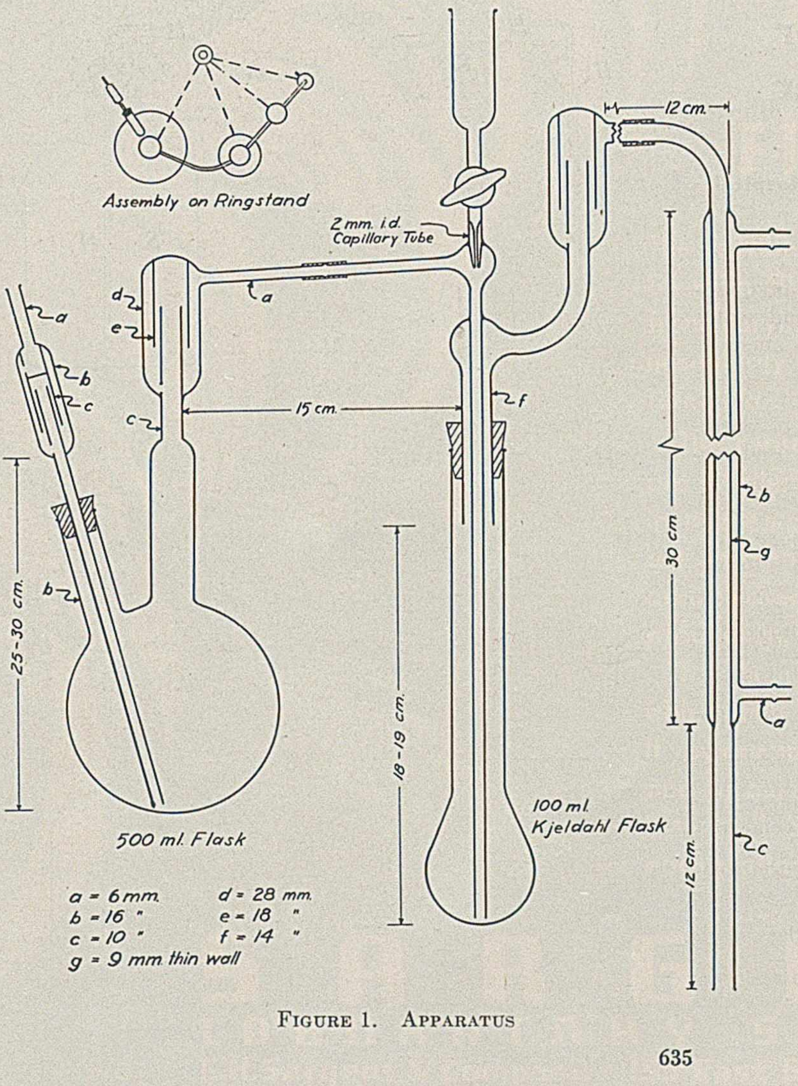

FIGURE 1. APPARATUS

Table I. Test Runs on Kjeldahl Distillation Apparatus

Time of Distillation	Nitrogen Found	Nitrogen Present	Error	Deviation from Mean of Group
Min.	*Mg.*	*Mg.*	%	%
8	12.47	12.42	+0.4	+0.2
8	12.43	...	+0.08	−0.08
7	12.42	...	0.00	−0.16
7	12.42	...	0.00	−0.16
6	12.43	...	+0.08	−0.08
6	12.47	...	+0.4	+0.2
6	3.094	3.110	−0.5	−0.2
6	3.107	...	−0.1	+0.1
6	3.104	...	−0.2	−0.06
6	0.627	0.625	+0.3	0.0
6	0.629	...	+0.6	+0.3
6	0.627	...	+0.3	0.0
6	0.624	...	−0.2	−0.5

the course of 1 to 2 minutes, slowly enough to avoid excessive heating. (If a mercury catalyst has been used 1 to 2 ml. of 1 *M* sodium sulfide solution should be added immediately after the sodium hydroxide.) The burner is then replaced under the Kjeldahl flask and the two burners are so adjusted that 40 to 50 ml. of distillate collect in 10 to 12 minutes. If bumping starts, the burner under the Kjeldahl flask is turned out and the other one is increased. After 8 to 10 minutes the receiver is lowered and 5 to 10 ml. of additional distillate are collected, the lower end of the condenser being above the surface of the solution in the flask. The acid in the receiver is then titrated in the usual manner.

Performance

To test the performance of the apparatus a standard solution of ammonium sulfate was used, so that no error due to incomplete digestion would be introduced. The data in Table I show the excellent performance of this apparatus, even with much shorter periods of distillation than those recommended and with samples containing as little as 0.6 mg. of nitrogen in the form of ammonium sulfate. This series of determinations represents a complete group of test distillations. No results were omitted because of inaccuracy. To make sure that the standard acid could not be sucked back, in several determinations the burners were turned off while the apparatus was in the midst of a distillation. No sucking back occurred in any part of the apparatus.

Summary

Directions are given for constructing and operating a semimicro-Kjeldahl distillation apparatus embodying the following advantages: one flask only for digestion and distillation; standard acid not subject to sucking back; apparatus compact and portable; and ammonia not liberated until apparatus is air-free.

The precision on samples containing as little as 0.6 mg. of nitrogen indicates that this apparatus may be used even on a micro scale.

Literature Cited

(1) Miller, H. S., Ind. Eng. Chem., Anal. Ed., 8, 50 (1936).
(2) Schulek, E., and Vastagh, G., *Z. anal. Chem.*, 92, 352 (1933).
(3) Sreenivasan, A., and Sadasivan, V., Ind. Eng. Chem., Anal. Ed., 11, 314 (1939).

Contribution 719, California Institute of Technology.

Constant-Level Still for Redistillation of Water

D. A. WILSON and H. S. STRICKLER
Endocrine Laboratory, Elizabeth Steel Magee Hospital, Pittsburgh, Penna.

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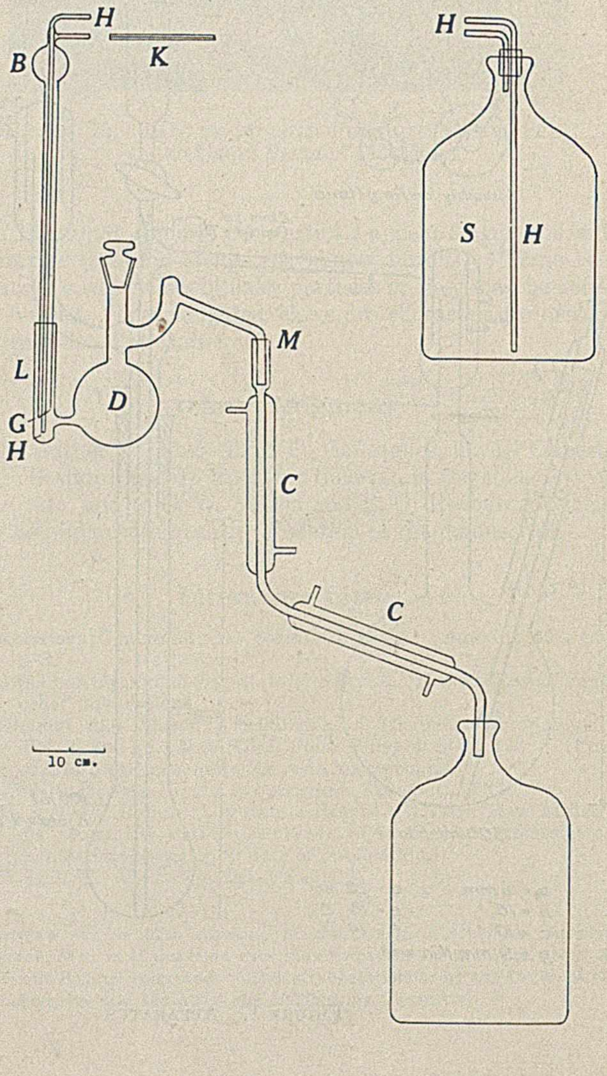
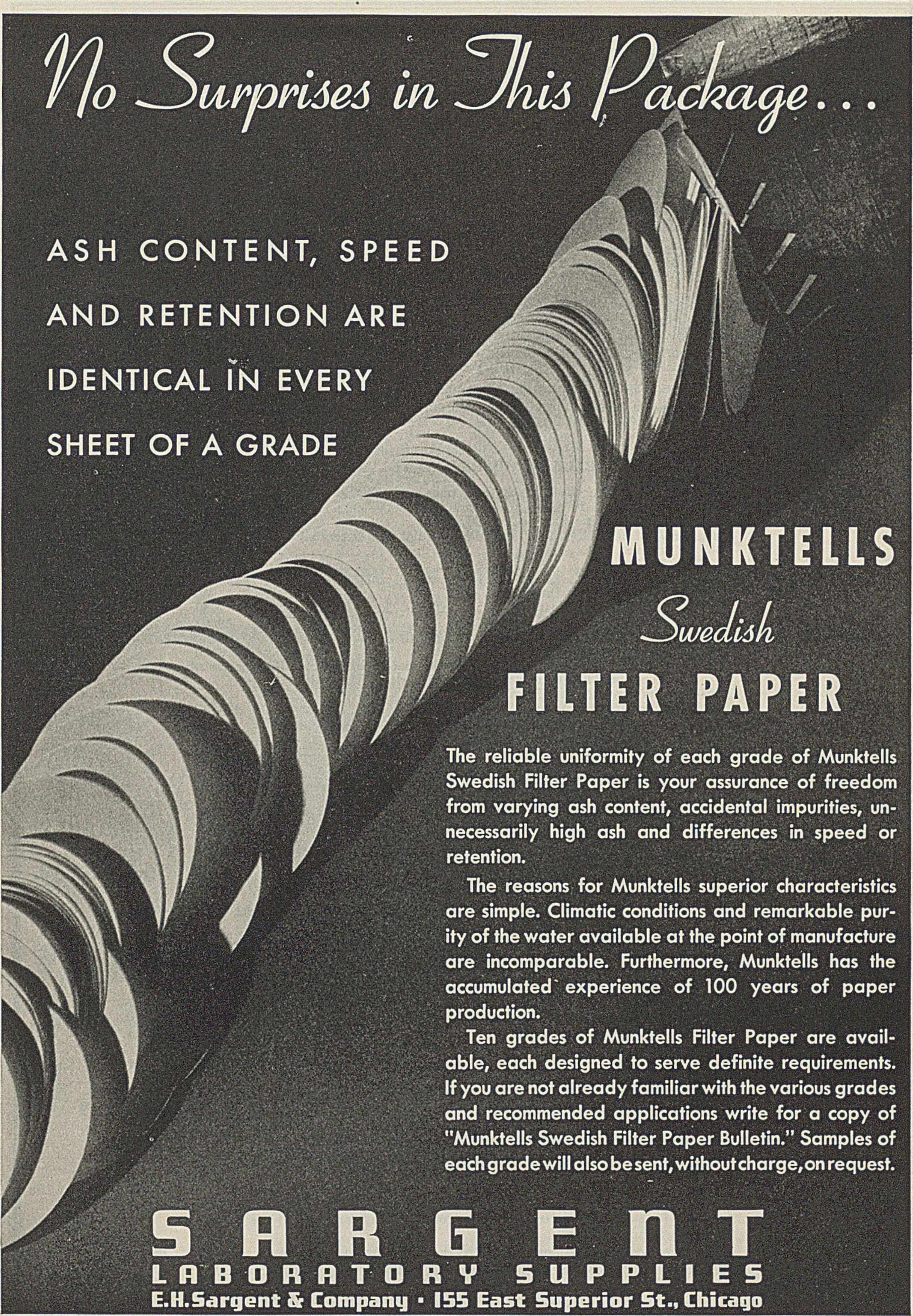


The figure is drawn to scale, as indicated. Water is boiled in a modified 1-liter Claisen flask, *D*, with two or three beads to prevent bumping, and is condensed in the double condenser, *C*, *C*. When the level of water in *D* drops below any point predetermined by the height to which *G* is set, air passes up through the water in the outer column to the safety bulb, *B*, and thence through the capillary, *K*, to the reservoir bottle, *S*. This starts the flow of water through the siphon tube, *H*. The flow continues until the end of *G* is again covered with water and the water in *G* is in hydrostatic equilibrium with that in reservoir *S*. The purpose of capillary *K* is to introduce an appreciable lag in the flow of water into flask *D*, so that in no case does the water cease boiling. The condenser bore must not be appreciably smaller than the outlet, *M*. Thus, with a coil-type condenser the constant-level device did not function. Although any condenser meeting the above requirement may be used, the compact double condenser, *C*, *C*, is found to give adequate condensation.

To keep out dust, it is well to cover *L* with Pyrex glass wool. *M* may be closed entirely.

The apparatus may be mounted by using a rod frame against a laboratory shelf on which *S* sits, or by constructing a wooden stand.



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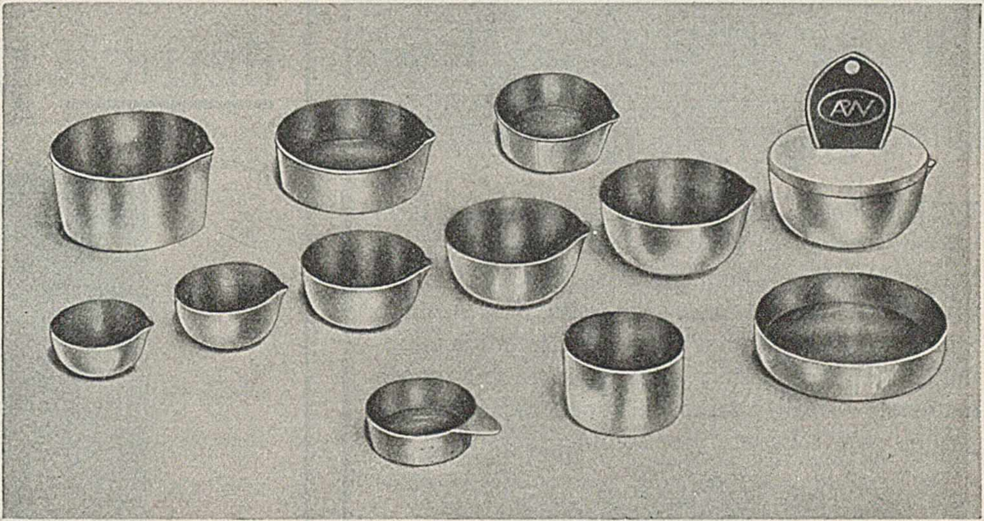

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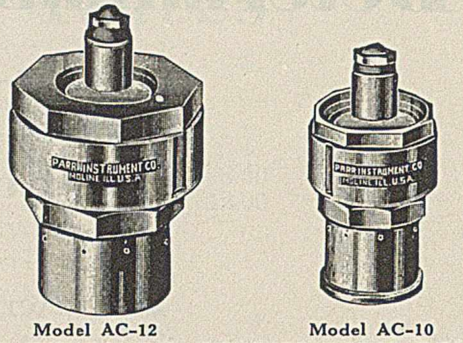
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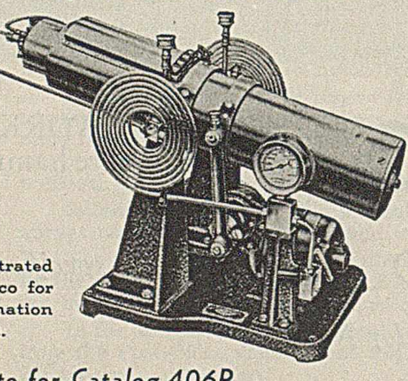

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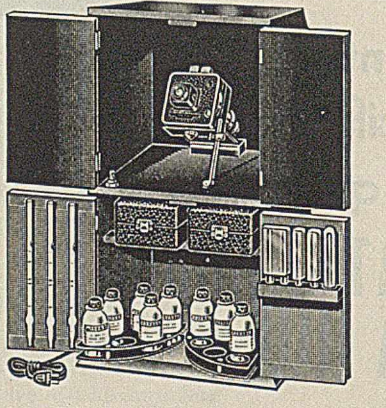

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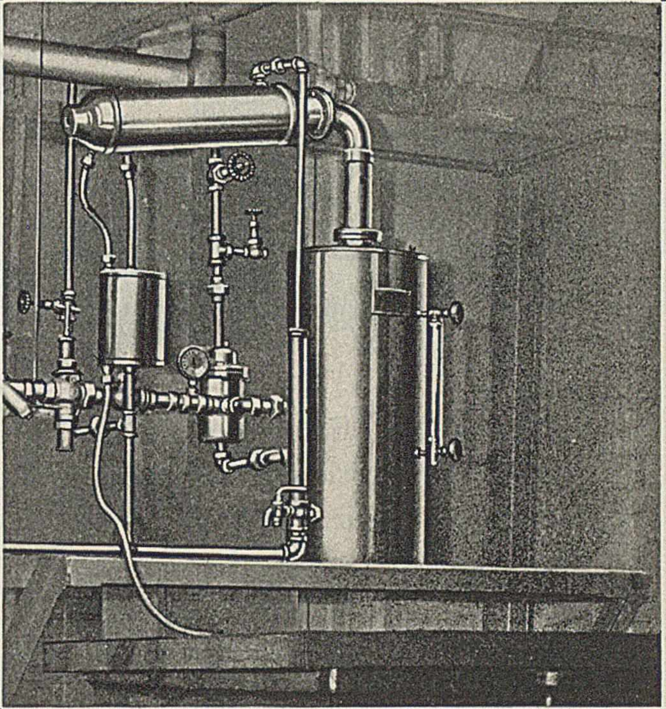

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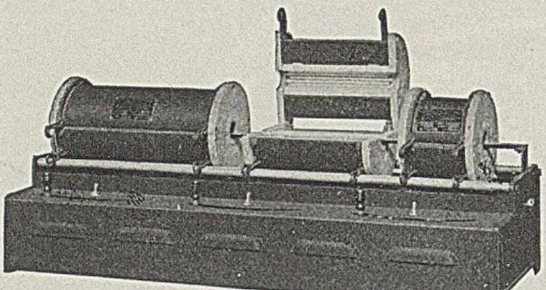

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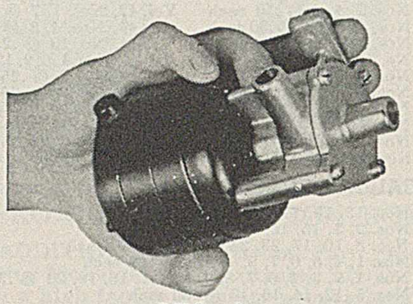

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