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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT
BEHAVIOR OF COPPER PHTHALOCYANINE PIGMENTS IN PAINT SYSTEMS

III. ACID PASTED CHLORINE-FREE CPC - CRYSTAL GROWTH AND FLOCCULATION OF THE ALUMINUM BENZOATE LAKE IN A LACQUER SYSTEM

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

BEHAVIOR OF COPPER PHTHALOCYANINE PIGMENTS IN PAINT SYSTEMS

III. ACID PASTED CHLORINE-FREE CPC - CRYSTAL GROWTH AND FLOCCULATION OF THE ALUMINUM BENZOATE LAKE IN A LACQUER SYSTEM

AUGUST 1949 - AUGUST 1950

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I. INTRODUCTION

A previous report, KN-50-18, made the observation that loss in CPC pigment strength for lacquer and alkyd systems is due to both changes in degree of flocculation and to crystal growth. Flocculation plays such an important role that in all cases investigated except for the acid pasted chlorine-free CPC, it completely overshadows the effect of crystal growth. This present investigation was designed to show that some separation between the effects of flocculation and crystal growth could be had by working with the aluminum benzoate lake where the flocculation effect was slight. This would lead to a clearer understanding of the role of crystal growth in the loss in pigment strength. A typical acid pasted chlorine-free CPC aluminum benzoate lake was used for this experiment.

II. CONCLUSIONS

1. Crystal growth of the aluminum benzoate lake of an acid pasted chlorine-free CPC in a lacquer system at 50°C is very pronounced and, over a period of 26 weeks, can account for a loss in pigment strength of around 75%.

2. The degree of flocculation of the aluminum benzoate lake is always low but sufficiently high to measure. It decreases during the early aging of the lacquer (8 weeks), after which it increases. This follows the pattern of the other CPC pigmented paint systems reported in KN-50-18.

3. There is some evidence that in the presence of TiO_2 extender crystal growth is inhibited.

III. EXPERIMENTAL

A. PREPARATION OF LACQUERS

1. CPC Lacquer

A pulp sample of Orchem's MDD-1643 Press Cake D-6624 was converted to the aluminum benzoate lake. This preparation followed the normal procedure for BL-282-D (C Process) and a 750 g sample (157.6 g dry basis) was used. The aluminum benzoate lake was coded 1285-8C.

A KV-36 lacquer grind was prepared according to the following outline.

Size of mill	1 gal
Pigment (1285-8C)	210 g
Grinding Vehicle (KV-36-GV)	1125 g
Thinning Vehicle (KV-36-TV)	525 g
Steel Balls (Size 3/16")	9300 g
Ball mill for	72 hrs.
Add KV-36-TV	1035 g

Strain off balls and store in two 1 qt. cans.

2. TiO_2 Lacquer

The white pigment used was "Ti-Pure", R-610 grade. The lacquer was made according to the following outline.

Size of mill	2 gal.
TiO_2 ("Ti-Pure", R-610 grade)	420 g
Grinding Vehicle (KV-36-GV)	2250 g
Thinning Vehicle (KV-36-TV)	1050
Porox balls (3/16")	A quantity sufficient to break the surface of the liquid
Ball mill for	72 hrs.
Add KV-36-TV	2070 g

Strain off balls and store in one quart cans.

B. STORAGE OF LACQUERS, PREPARATION OF EXTENSIONS AND PANELS

The CPC lacquer was stored in two one-quart cans at room temperature for three weeks and then at 50°C (122°F) up to a total time of 26 weeks. The TiO_2 lacquer was stored at all times at room temperature in one quart cans.

From time to time, samples of the CPC lacquer were withdrawn and extensions made with the TiO_2 lacquer. Before any lacquer was withdrawn from any of the cans they were first shaken from 10 to 30 min. in a shaking device called a "Paint Rejuvenator", manufactured by the Miracle Paint Rejuvenator Co. After the cans were opened, the contents were inspected for uniformity by manipulation with a spatula. Good uniformity was always found.

All extensions were made in duplicate. To make the extensions, a 22.24 g portion of the CPC lacquer was mixed with a 100.0 g portion of the white lacquer. This gave a 10/90 toner basis extension (20/90 on lake basis). The mixing was accomplished by first stirring with a "Lightnin" mixer for 15 min. and then shaking for 15 min. on the "Rejuvenator". This shaking and mixing schedule assured a uniform extension and assured an unchanging composition of the lacquer in the can which meant a reliable estimate of the CPC/TiO_2 ratio. It is true, however, that small variations in the CPC/TiO_2 ratio can be tolerated because of the spectrophotometric method of expressing the results.

These extensions were thinned to spraying consistency (1:1) with T-3601. Primed aluminum panels 3" x 7" were sprayed in the conventional manner. An attempt was made to keep spraying conditions reasonably constant throughout the experiment. After the sprayed panel had dried, a portion of the spatula-stirred thinned lacquer was poured over the panel, covering approximately 1/3 to 1/2 of the panel. The panel was then tipped on edge and the excess lacquer allowed to drain off. This is the conventional practice for making the so-called "pour out" test. This surface was then allowed to dry.

C. OBTAINING LIGHT REFLECTANCE CURVES

A G.E. self-recording spectrophotometer was used. The reflectance was recorded relative to the National Bureau of Standards Vitrolite White. All reflectance measurements were made exclusive of the specular beam. On the G.E. instrument, this is accomplished by inserting black velvet cups in the integrating sphere. The complete curve from 400 mμ to 700 mμ was obtained for all panels but for calculations, only the reflectance at 465 mμ and 616 mμ was used. These reflectances were corrected to a MgO white basis using the conversion factors supplied by the Bureau of Standards. Curves were obtained for both the sprayed portion and the poured portion of the panel.

D. CONVERSION OF REFLECTANCE CURVES TO FLOCCULATION AND CRYSTAL GROWTH DATA

1. Measurement of Flocculation

For the measurement of flocculation, the spectrophotometric curves of both the sprayed and the poured portions of the panel were used. If no flocculation existed, both surfaces would yield the same curve and the flocculation index would be zero. If crystal growth had occurred, it would not become a part of the flocculation measurement because the crystal size would be the same for both the sprayed portion and the poured portion. If a flocculation difference existed, the flocculation index Δb was calculated from the following equation, the development of which is explained in KN-50-15:

$$\Delta b = 30\,\Delta\phi_2 - \Delta\phi_1$$

Δb = a term which increases in magnitude when there is a relative increase in average particle size, in this case an increase in flocculation.

30 = Estimate of the constant slope of the straight line obtained by plotting ϕ_1, as ordinate and ϕ_2 as abscissa for a series of extensions.

$\Delta\phi_1$ = the difference in ϕ_1 values derived at a wave-length of 465 mμ between the sprayed and poured surfaces.

$\Delta\phi_2$ = the difference in ϕ_2 values derived at a wave-length of 616mμ between the same two colored surfaces.

Note: The subtraction of ϕ values of the two colored surfaces to obtain $\Delta\phi$ was always made poured minus sprayed.

$\phi = \frac{2R}{(1-R)^2}$ where R is the reflectance exclusive of the specular reflectance and corrected to MgO white as the reference white.

The following is a typical calculation using data derived from the spectrophotometric curves of one of the panels.

	Masstone Lacquer Aged Three Weeks					
	λ = 465 mμ			λ = 616 mμ		
Panel Surface	**% R**	**%R(Corr.)**	ϕ_1	**% R**	**%R(Corr.)**	ϕ_2
Poured	57.9	50.4	4.10	10.2	8.89	0.214
Sprayed	57.0	49.6	3.91	9.6	8.36	0q199
		$\Delta\phi_1$ =	+0.19		$\Delta\phi_2$ =	+0.015

$$\Delta b = 30\,\Delta\phi_2 - \Delta\phi_1$$

$$\Delta b = 30\,(0.015) - 0.19$$

$$\Delta b = +0.26$$

Note: A large positive value indicates considerable flocculation. A low or negative value means very little flocculation. In this case, the numerical value of +0.26 means very little flocculation.

2. Measurement of Crystal Growth

With age of the lacquer, the appearance of the sprayed portion of the TiO_2 extension changed. Both flocculation and crystal growth can be responsible for this change. With an aluminum benzoate lake however, the flocculation is small and the bulk of the change can be attributed to crystal growth. For this experiment, for the sake of simplicity, the index derived from a comparison of the initial panel with with the aged panel will be called the "crystal growth" index. The same function is used to calculate the crystal growth index as that used to calculate the flocculation index but instead of comparing a sprayed with a poured surface, the surface of an aged lacquer is compared with the surface of a fresh lacquer. To distinguish the index from the flocculation index, it will be called $\Delta\rho$ and the equation becomes $\Delta\rho = 30\ \Delta\phi_2 - \Delta\phi_1$ where $\Delta\phi_1$ is derived from the "aged" measurement minus the "initial" measurement at 465 mμ, and $\Delta\phi_2$ is derived from the aged measurement minus the initial measurement at 616mμ.

The following is a typical calculation from data derived from the spectrophotometric curves of one of the panels.

Sprayed Surface	λ = 465 mμ			λ = 616 mμ		
	% R	%R(Corr.)	ϕ	% R	%R(Corr.)	ϕ
5 wks. aged lacquer	58.7	51.2	4.30	12.3	10.7	0.269
Initial lacquer	57.5	50.0	4.00	9.4	8.2	0.195
			$\Delta\phi_1 = 0.30$			$\Delta\phi_2 = 0.074$

$$\Delta\rho = 30\ \Delta\phi_2 - \Delta\phi_1 = 1.92$$

Note: A large positive value indicates considerable crystal growth. In this case the numerical value of 1.92 indicates a moderate amount of crystal growth.

E. COMPILATION OF DATA

Both the flocculation data and the crystal growth data are recorded in Table 1.

Table 1

CPC - Al Benz. Lake

Time (Weeks)	Lacquer Flocculation Index	Lacquer Crystal Growth Index	Remarks
0	0.81	--	(Room Temp. storage
3	0.26	0.21	(from 0 to 3 weeks.
5	-0.25	1.92	(After 3 week reading
6	-0.20	3.59	(subsequent storage (was at 50°C.
7	-0.33	5.06	Second Can of TiO_2 used.
8	-0.82	5.59	
8	-0.84	7.24	Second Can of CPC used.
26	0.20	8.71	
* 26	0.36	4.42	

* These data are derived from reflectance curves of the

* These data are derived from reflectance curves of the aged extension and not the aged masstone. The essential difference between this and the other 26 week panel is that in one case the CPC aged in the absence of the extender and in the other case it aged in the presence of the extender.

Fig. 1. plots the data of Table 1. A detailed discussion of this plot will be deferred to the section on general discussion.

F. ELECTRON MICROGRAPHS

At intervals during the aging of the enamel, electron micrographs were obtained of the unextended lacquer. These are listed below and are illustrated in Figures 2 through 5. They will be discussed in greater detail in the next section.

			Aging Schedule of Lacquer
Fig. 2	Plate	1152	19 days at room temp.
3	"	1161	3 weeks at room temp. + 2 weeks at 50°C
4	"	1167	3 " at room temp. + 3 weeks at 50°C
5	"	1233	3 " at room temp. + 23 weeks at 50°C

IV. GENERAL DISCUSSION

A. DESCRIPTION AND LIMITATIONS OF INDICES

Two indices have been defined (see section III-D) based on light reflectance curves. One index, the flocculation index, is based on the difference between the curve appearance of a sprayed and poured lacquer surface. The seemingly complicated method of expressing the index is justified because when so expressed it is insensitive to small changes in ratio of CPC to TiO_2 . This makes unnecessary extreme precision in making extensions for comparison purposes.

Unfortunately this index is not completely insensitive to factors other than changes in flocculation of the CPC. It is probably somewhat sensitive to changes in flocculation of TiO_2 . With regards to flooding, it is reasonably insensitive to changes in ratio of CPC to TiO_2 brought about through flooding but if the flooding mechanism causes a separation of fine particles from course particles as well as a change in pigment ratio, the magnitude of the index will be affected. At best, it must be recognised that the index measures a composite of several factors but these self-same factors are also included in our visual interpretation of flocculation. In other words, "flocculation" is fairly rigidly defined as "the formation of clusters of particles separable by weak forces" but our visual interpretation of a flocculated system also includes the phenomena of "floating", "flooding", and "pigment separation". This "flocculation index" takes a step in the direction of achieving some separation of these other phenomena but the separation is by no means complete. Recognising that other factors do have some effect on the magnitude of the index, for the sake of simplicity, it will still be called a "flocculation" index.

The other index utilised in this report is the so-called "crystal growth" index. It is also derived through comparison of two colored surfaces but, in this case, the colored surfaces are an initial and an aged surface. This index is calculated in the same manner as the "flocculation" index and like it, is relatively insensitive to small changes in the ratio of CPC to TiO_2. The crystal growth index is admittedly also dependent on changes in degree of flocculation but in this experiment flocculation is low and crystal growth is high. Furthermore the act of spraying tends to give a deflocculated and rapid drying surface which will further minimise the already small flocculation effect. Because the other factors affecting the index are small, for the sake of simplicity it is justified to call this the crystal growth index.

B. DATA INTERPRETATION

Figure 1 gives a complete description of the aging study of this lacquer system. In interpreting the two curves it must be borne in mind that the Δb values for flocculation bear no direct relationship to the Δc values for crystal growth. Numerical values are not to be compared but it is valid to compare the directions taken by the curves. It should also be recognised that the precision in the flocculation measurement is poor, being around 0.3 Δb and the values, which are small, are simply used to indicate a trend. This they very clearly do. The precision of the crystal growth measurement is somewhat better, being around 0.2 Δc.

Referring to Figure 1, it is seen that at room temperature aging up to three weeks, there is very little evidence of crystal growth although flocculation is falling off. The electron micrograph (Fig. 2) also shows no crystal growth. At the end of three weeks, 50°C aging was begun and the crystal growth curve takes a sharp turn upward. The electron micrograph (Fig. 3) now shows evidence of crystal growth. The flocculation index is still falling off. It is evident from a comparison of the two curves where one is rapidly rising and the other is falling off, that the change in flocculation is not greatly influencing the crystal growth index. This is one of the assumptions made, and hence, for this experiment, it appears justified. This is undoubtedly due to the fact that the crystal growth is so very much greater than the change in flocculation.

The steep rise in the crystal growth curve continues until about 8 weeks aging at which time it tends to level off. The electron micrographs also show that crystal growth is quite active over that period of time. In comparing the micrographs it should be kept in mind that Fig. 2 is at 35,000 X magnification whereas the remaining micrographs are at 3,500 X magnification.

In the interval of 5 to 8 weeks it became necessary to start examining fresh cans of lacquer. The 7th week readings and all subsequent readings were made on tints using the second can of TiO_2 lacquer. For the 8th week readings, the second can of CPC lacquer was started. Fig. 1 shows the 8th week readings for both the first and second cans of CPC lacquer. From Fig. 1 it can be seen that the flocculation index was not affected by the change of cans. The two points are well within experimental error. This is not the case, however, with the crystal growth index. The second can of CPC lacquer showed a significantly higher crystal growth index than the first can. It is entirely possible that the two cans got off to a different crystal growth start. This can be expected when comparing crystal growth in two isolated systems. This would be particularly noticeable in the steep portion of the curve.

At the termination of the experiment after 26 weeks aging, a panel was prepared of the initial tint which had been aging at the same temperature as the masstone lacquer. This enabled a comparison of the effect of age on a CPC lacquer in the presence and absence of the TiO_2 extender. Figure 1 shows these points. At 26 weeks, the aged tint has about the same flocculation index as the fresh tint. The difference in the position of the points is too close to the precision of the measurement to be considered significant. The crystal growth index, however, presents a different picture. The aged tint shows far less evidence of crystal growth than the aged masstone lacquer. This strongly suggests that the presence of TiO_2 inhibits crystal growth.

There can be no doubt that the major change in this lacquer system is one of crystal growth with the attendent loss in pigment strength. The $\triangle c$ index is not to be considered as a simple function of pigment strength, so strength in this case had best be judged by visual inspection of the panels. Such an inspection indicates that over the period of 26 weeks, the strength loss has been at least 75%.

V. FURTHER RESEARCH

Work has already been completed on a similar investigation using an acid pasted LB type and an acid pasted semi-chlor type of CPC in place of the acid pasted chlorine-free type used for this report. These types have also been observed to grow crystals in paint systems but to a lesser degree than the acid-pasted chlorine-free type. The results will be given in another report.

ACKNOWLEDGEMENT

The preparation of all lacquers as well as the preparation of all extensions and the spraying of all panels were done by the "Pigment Evaluation Group" under the direction of Mr. B. J. Godfrey.

A. R. HANKE
CHEMICAL DIVISION

ARH:lg
Att.

Figure 2.

Lacquer aged 19 days at room temperature

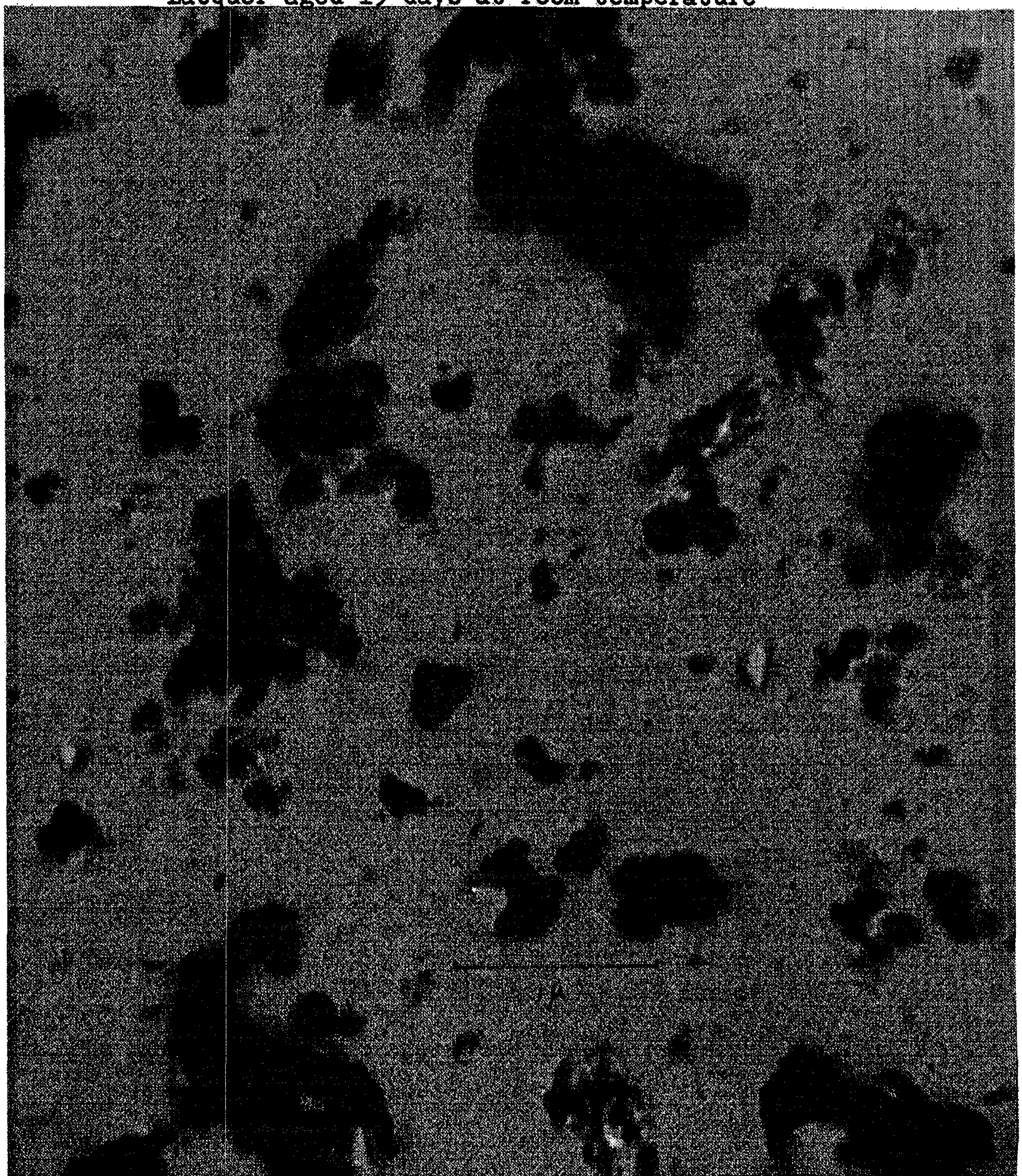

Plate 1152 35,000 X

Figure 3.

Lacquer aged 3 weeks at room temperature + 2 weeks at 50°C

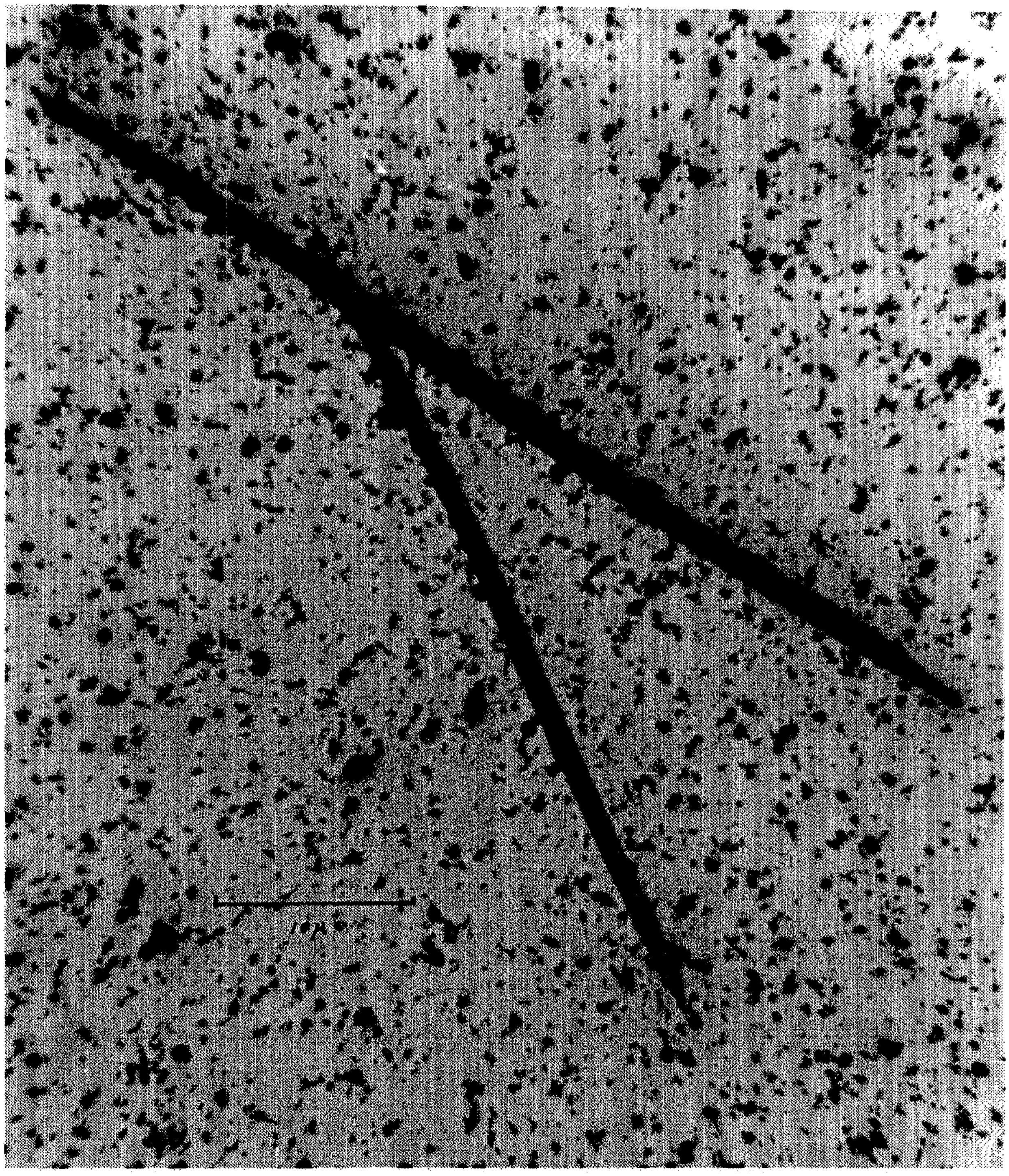

Plate 1161 3,500 X

Figure 4.

Lacquer aged 3 weeks at room temperature + 3 weeks at 50°C

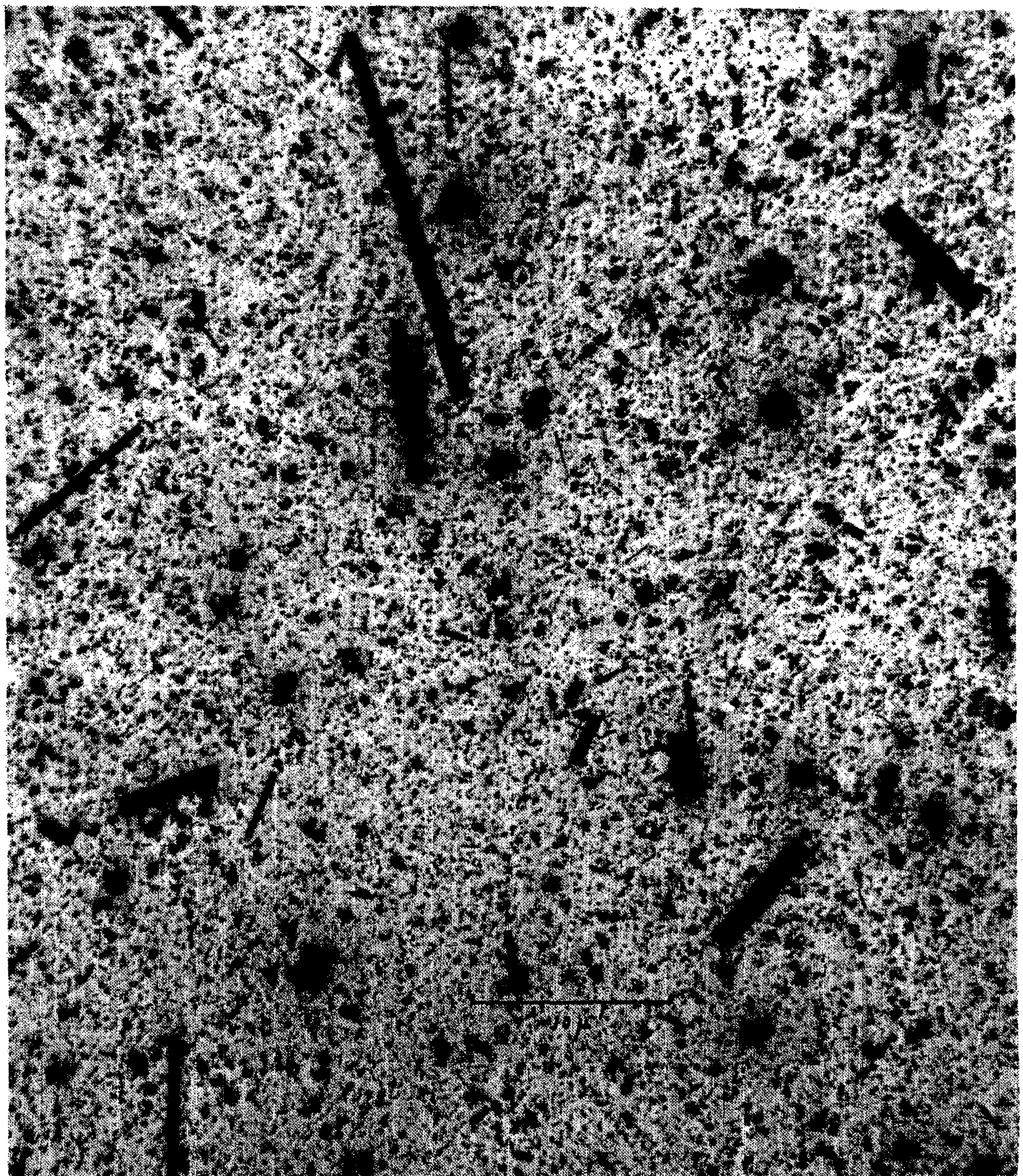

Plate 1167 3,500 X

Figure 5.

Lacquer aged 3 weeks at room temperature + 23 weeks at 50°C

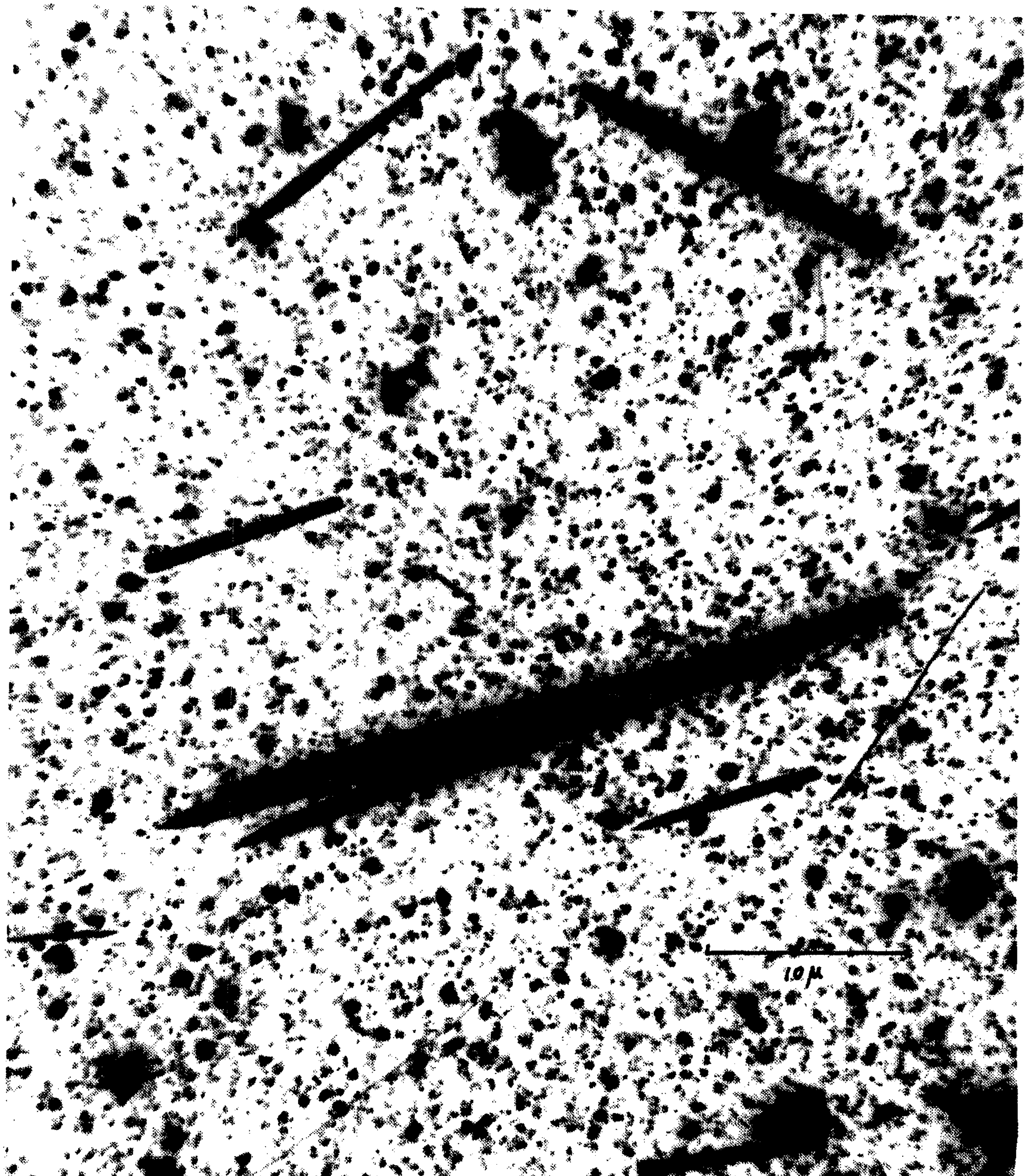

Plate 1233 3,500 X