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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT
Final Report

BEHAVIOR OF COPPER PHTHALOCYANINE PIGMENTS IN PAINT SYSTEMS

IV. ACID PASTED LB AND SEMICHLOR -FLOCCULATION AND CRYSTAL GROWTH OF THE ALUMINUM BENZOATE LAKES IN LACQUER.

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IV. ACID PASTED LB AND SEMI-CHLOR -FLOCCULATION AND CRYSTAL GROWTH OF THE ALUMINUM BENZOATE LAKES IN LACQUER.

NOVEMBER 1949 TO DECEMBER 1950

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I. INTRODUCTION

In a previous report (KN-51-40), spectrophotometric reflectance curves and electron micrographs were used to show that considerable crystal growth of an acid pasted chlorine-free CPC occurred in a lacquer system and that this crystal growth resulted in considerable loss of pigment strength. It has also been previously observed (KN-50-16) that two other acid pasted CPC pigments containing some chlorine can also become crystalline under similar conditions, but the tendency toward crystal growth is less. Previous attempts to associate the small amount of crystal growth of these pigments with loss in pigment strength have failed because strength changes due to changes in degree of flocculation were always more pronounced and tended to overshadow the strength changes produced by crystal growth alone.

This report deals with the attempt to assess the loss in pigment strength, due to crystal growth alone, of an acid pasted semichlor CPC of Orchem manufacture containing 3.30% Cl and a so-called acid pasted LB/CPC of Orchem manufacture containing 3.41% Cl. In order to accomplish this, the effect of changes in degree of flocculation is minimized by working with the aluminum benzoate lakes, in which form the flocculation is slight.

It should be pointed out that the sample of Orchem's LB/CPC chosen for this work does not contain as much chlorine as the LB type pigment of Newark manufacture. The Newark type contains around 4.4% chlorine. It should also be pointed out that this sample of Orchem's semi-chlor CPC contains more chlorine than the average semi-chlor product which runs about 2.9% Cl. This brings the two samples quite close in chlorine content and it can be expected that the crystal growing characteristics of the two pigments will be similar which indeed they are.

II. SUMMARY AND CONCLUSIONS

1. Lacquers of aluminum benzoate lakes of the acid pasted LB/CPC (3.41% Cl) and semi-chlor CPC (3.30% Cl) used for this experiment, when stored at 50°C show a small amount of rapid crystal growth within the first few weeks.

2. The loss in strength brought about by this rapid growth is balanced by a gain in strength brought about by a rapid decrease in flocculation, which tends to keep the strength about the same. If degree of flocculation had remained constant, the crystal growth observed within the first few weeks would have caused a decrease in pigment strength.

3. After the initial rapid crystal growth, there is a slight decrease in pigment strength which is not due to a change in flocculation. The electron micrographs do not clearly show this change as due to crystal growth. It is possible that pigment aggregation is occurring due to changes in the resin solids of the vehicle. To support this contention, it was observed that as aging progressed, it was increasingly difficult to prepare adequate dispersions for the electron micrographs.

4. The rather rapid decrease in flocculation observed during the first week of aging, and which has been previously observed for other CPC lacquers (see KN-50-18), has been ascribed to the "wetting out" of the paint. Another reasonable explanation is

that the addition of thinning vehicle after the grind, creates a more compatible balance between solvent and resins and that the establishment of this new equilibrium results in a decrease in the pigment flocculation measurement. There is some similarity between this phenomenon and "Reactivity".

III. EXPERIMENTAL

A. Preparation of Lacquer

1. CPC Lacquers

The semi-chlor CPC was derived from BK Paste Lot 469 (N-493) containing 3.30% Cl. The aluminum benzoate lake was prepared according to the normal procedure for BL-282-D (C Process) and a 2820 g sample (158 g dry basis) was used. This yielded 320 grams dry lake. The sample was coded 1285-8D.

The acid pasted LB/CPC was derived from Orchem's MDD-1156 HT. This is a sample of Orchem manufacture made by the solvent (TCB) reaction process using phthalic anhydride and contains 3.41% Cl. The aluminum benzoate lake was prepared from 635 g of pulp (88.8 g dry basis). This yielded 158 g dry lake and the sample was coded 1285-8E. Both pigments were micropulverized and KV-36 lacquers were prepared according to the following outline:

	1285-8D	1285-8E
Size of mill	1/3 gal.	1/3 gal.
Pigment	90 g.	90 g.
Grinding vehicle (KV-36-GV)	450 g.	450 g.
Thinning vehicle (KV-36-TV)	210 g.	210 g.
Mixed steel balls (3/16" - 5/8")	1 pt.	1 pt.
Grind for	72 hrs.	72 hrs.
Strain off balls and obtain yield		
Mill base yield	649 g	617 g
Add KV-36-TV	358 g	341 g
Mix and store in 1 gal. cans.		

This gave a pigmentation of 7.73% in each case.

2. TiO_2 Lacquer

The white pigment used for extensions was "Ti-Pure" R-610 grade. Two 1 gal. grinds were prepared according to the following outline.

	1	2
Size of mill	1 gal.	1 gal.
Pigment (R-610)	708 g	708 g
Grinding vehicle (KV-36-GV)	1350 g	1350 g
Porox balls (3/8")	1 qt.	1 qt.
Grind for	72 hrs.	72 hrs.
Strain off balls and obtain yield		
Mill base yield	4060 g	
Add thinning vehicle (KV-36-TV)	3700 g	

Mix and split into 2 equal portions
Store in two 1 gal. cans. This gave a pigmentation of 18.02%

B. Storage of Lacquers, Preparation of Extensions and Panels

The two, one gal. cans containing each type of CPC were stored in an oven at 50°C (122°F) for a period of 1 year. The cans of TiO_2 lacquer were stored at room temperature. From time to time, the cans were removed from the oven and 10/90 extensions (toner basis) were made using the TiO_2 lacquer. Since the TiO_2 lacquer was stored in two cans, one can was always used for semi-chlor extensions and the other can for LB extensions.

Before opening, the cans were first shaken for 10 min. to 30 min. in a shaking device manufactured by the Miracle Paint Rejuvenator Co. The cans were then opened and the lacquer inspected for uniformity by manipulation with a spatula. Good uniformity was always found.

To make the extensions, a 38.8 gram portion of the CPC lacquer was mixed with a 75 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 assured a uniform lacquer and an unchanging composition of the lacquer in the can, which meant reasonable duplication of the degree of extension. Early experiments had shown the need for such treatment in achieving the necessary uniformity for the kind of tests subsequently made.

These extensions were thinned to spraying consistency with T-3601 (1:1 by volume). 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. Light Reflectance Curves

A G.E. self-recording spectrophotometer was used. The reflectance was recorded relative to the National Bureau of Standard 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 $m\mu$ to 700 $m\mu$ was obtained for all panels but for calculations, only the reflectance at 465 $m\mu$ and 616 $m\mu$ 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 616 mμ 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.

ACID PASTED LB MASSTONE LACQUER AGED 3 WEEKS

PANEL SURFACE	λ = 465 mμ			λ = 616 mμ		
	% R_1	% R_1 (Corr.)	ϕ_1	% R_2	% R_2 (Corr.)	ϕ_2
Poured	59.6	52.0	4.48	10.3	8.98	0.217
Sprayed	59.6	52.0	4.48	9.0	7.84	0.185
		$\Delta\phi_1$ =	0.00		$\Delta\phi_2$ =	0.032

$$\Delta b = 30\,\Delta\phi_2 - \Delta\phi_1$$
$$\Delta b = 30\,(0.032) - 0$$
$$\Delta b = 0.96$$

Note: A large value indicates considerable flocculation. A low value

Note: (Cont'd) means very little flocculation. In this case 0.96 means a low but significant amount of 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 if crystal growth is large most of the change with age can be attributed to crystal growth. This is the case with the acid pasted chlorine-free CPC described in KN-51-40. In the case of acid pasted LB and semi-chlor CPC, crystal growth is not large, hence if it is shown that flocculation is increasing with time it will be difficult to say whether the change is due to crystal growth or flocculation or both. In other words, an index sensitive to crystal growth alone is not possible with measurements described in this report. Since the index measuring crystal growth is also sensitive to flocculation, it will be called the crystal growth-flocculation composite index. Such an index is still useful in those cases where it can be shown that flocculation is decreasing and the composite index is increasing. In such a case, the increase cannot be due to flocculation.

The composite index uses the same function as the flocculation index but instead of comparing a sprayed with a poured surface as is done in the flocculation index, 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 Δc and the equation becomes $\Delta c = 30\,\Delta\phi_2 - \Delta\phi_1$ 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 616 mμ.

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

ACID PASTED LB MASSTONE LACQUERS

SPRAYED SURFACE	λ = 465 mμ			λ 616 mμ		
	% R_1	%R_1 (Corr.)	ϕ_1	%R_2	%R_2 (Corr.)	ϕ_2
3 wks. aged lacquer	59.6	52.0	4.48	9.0	7.84	0.185
Initial lacquer	60.3	52.5	4.66	9.0	7.84	0.185
		$\Delta\phi_1$ =	-0.18		$\Delta\phi_2$ =	0.000

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

$$\Delta c = 30(o) + 0.18$$

$$\Delta c = +\,0.18$$

Note: A large positive value indicates considerable composite crystal growth and flocculation. In this case, + 0.18 is so small that

Note:(Cont'd) it is of doubtful significance and may be within the experimental error.

E. Compilation of Data

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

TABLE 1

Time(Weeks)	ACID PASTED LB Flocculation Index	ACID PASTED LB Crystal Growth-Flocculation Composite Index	ACID PASTED SEMI-CHLOR Flocculation Index	ACID PASTED SEMI-CHLOR Crystal Growth-Flocculation Composite Index
0	2.28	0	1.98	0
1	0.81	0.03	1.08	0.12
2	1.02	-0.12	1.20	0.03
3	0.96	0.18	1.23	0.27
5	1.23	0.03	1.44	0.15
26	1.01	0.61	2.13	0.86
52	1.52	1.07	1.65	1.13

Note: By zero time in column 1 is meant the time at which the pigment has been ground into the vehicle. Since the grinding time is 72 hrs., it is in reality already 3 days old if reckoned from the time the vehicle touched the pigment. At zero time therefore, some crystal growth has already occurred.

The composite index has the numerical value of zero for zero time because the difference is reckoned from the zero time curve.

The data of Table 1 are plotted in Figure I.

F. Electron Micrographs

At the time the TiO_2 extensions were made to obtain spectrophotometric curves, electron micrographs were also obtained of the unextended lacquer. These are illustrated in Figures 2 through 11. They will be discussed in greater detail in the next section.

			ACID PASTED LB MASSTONE LACQUER AGED AT 50°C
Fig. 2	Plate	1189	Initial
3	"	1192	1 week
4	"	1202	5 weeks
5	"	1340	6 months
6	"	1424	1 year

			SEMI-CHLOR MASSTONE LACQUER AGED AT 50°C
Fig. 7	Plate	1188	Initial
8	"	1193	1 week
9	"	1201	5 weeks
10	"	1339	6 months
11	"	1423	1 year

IV. GENERAL DISCUSSION

A. Description and Limitations of Indices

Two indices have been defined (see Section III-D) based on light reflectance curves. The first 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 recognized 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. Recognizing 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 second index utilized in this report is the so-called "crystal growth-flocculation composite" 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. This index is the closest approach to a separation between the effects of flocculation and crystal growth that can be made with the data of this report. When flocculation is low, this index reflects the effect of crystal growth. For the data of this report, the flocculation is low because we are dealing with aluminum benzoate lakes but it is also true that for the pigments studied, crystal growth is also low and hence both the factor of flocculation and of crystal growth must be considered when dealing with this second index.

B. Data Interpretation

Fig. 1 shows that the tendency towards flocculation of these aluminum benzoate lakes falls off during the early aging period of the lacquer. After a few weeks, there is a reversal and following that a tendency for the flocculation curve to level off. This is exactly the pattern followed by the toners and reported in KN-50-18.

Another observation to make is that as flocculation is decreasing during the early aging period of the first few weeks, the composite measurement of crystal growth and flocculation remains about the same. It has previously been observed for crystal stable CPC (KN-50-18) that a decrease in flocculation would cause a decrease in this composite measurement but it is during this early aging period that crystal growth is occurring. See Figures 2, 3, 4, & 7, 8, 9. In fact, the electron micrographs show that in the case of the semi-chlor CPC, crystal growth has occurred during grinding and the crystals are clearly evident in the initial lacquer. This will tend to decrease pigment strength and the actual $\triangle$ c value will be the result of these two opposing conditions. During the later aging portion of the curve, the extent of flocculation is no longer changing rapidly, whereas pigment strength is still falling off to some extent. This would indicate continued crystal growth but such growth is not clearly evident from the electron micrographs. See Figures 2 through 11. These micrographs show that after an initial period of crystal growth, further growth is extremely slow. That crystal growth is responsible for the loss in strength during the later aging period must be considered with doubt. A form of aggregation may be responsible and it was noted that good dispersions for electron micrographs were more difficult to obtain with aged lacquers than with fresh lacquers.

V. PATENT SITUATION

No action is planned.

VI. FUTURE PROGRAM

This is the final report in the series of four reports and no further work is contemplated.

lg

Figure 1. Change in Flocculation and Crystal Growth

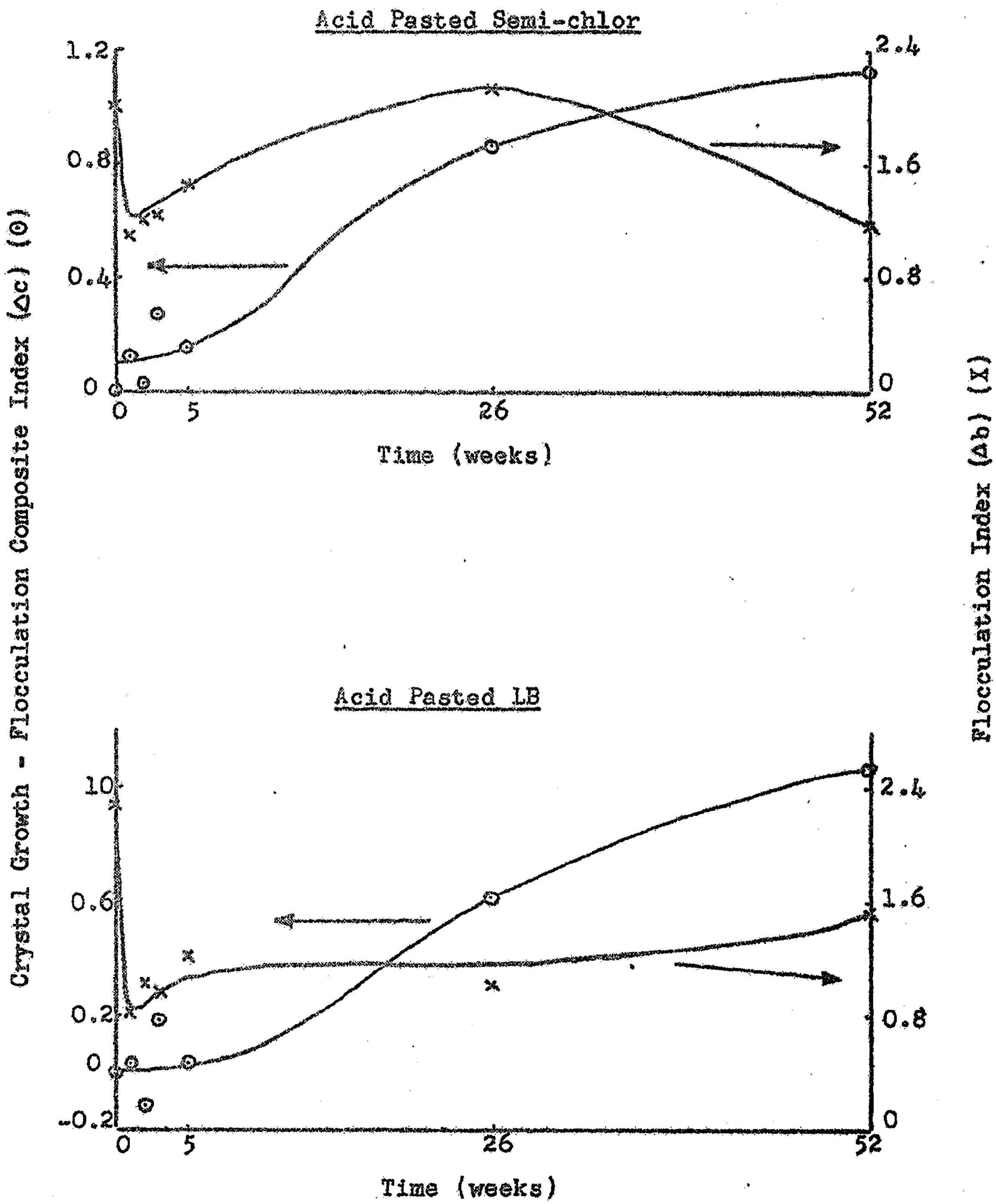

Figure 2. Initial Acid Pasted LB Masstone Lacquer

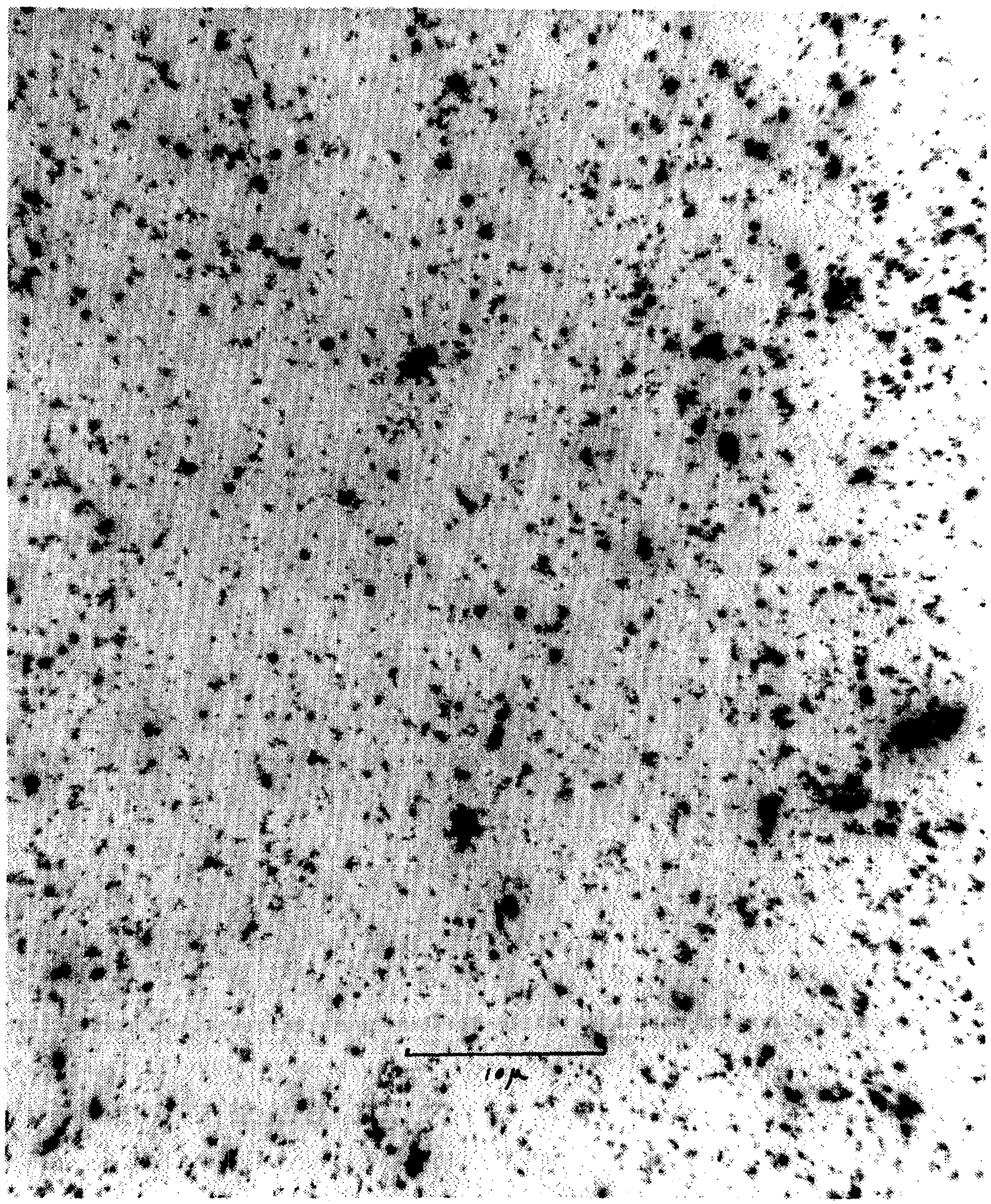

Plate 1189

3,500 X

Figure 3. Acid Pasted LB Masstone Lacquer

Aged 1 Week at 50°C

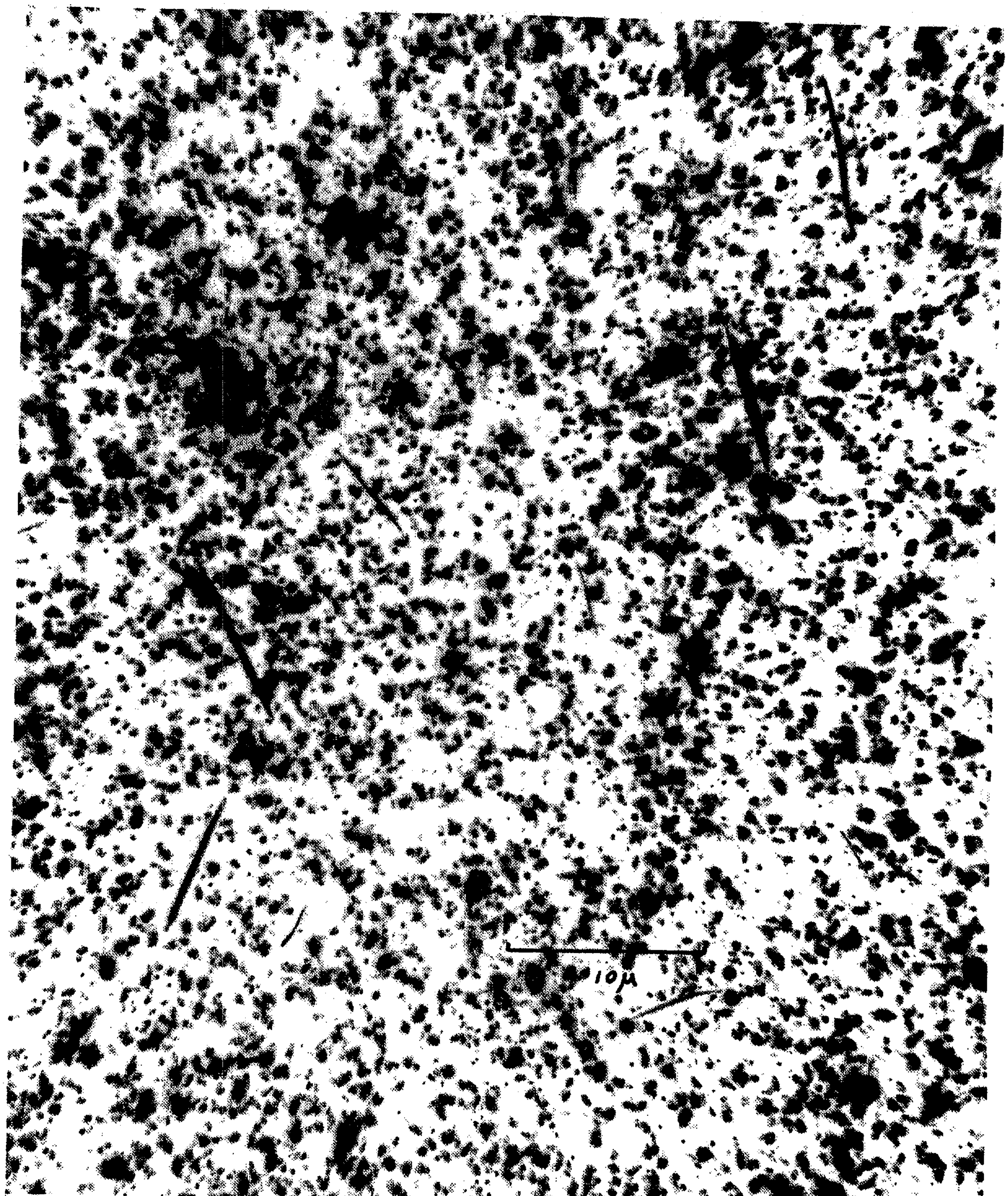

Plate 1192

3,500 X

Figure 4. Acid Pasted LB Masstone Lacquer

Aged 5 Weeks at 50°C

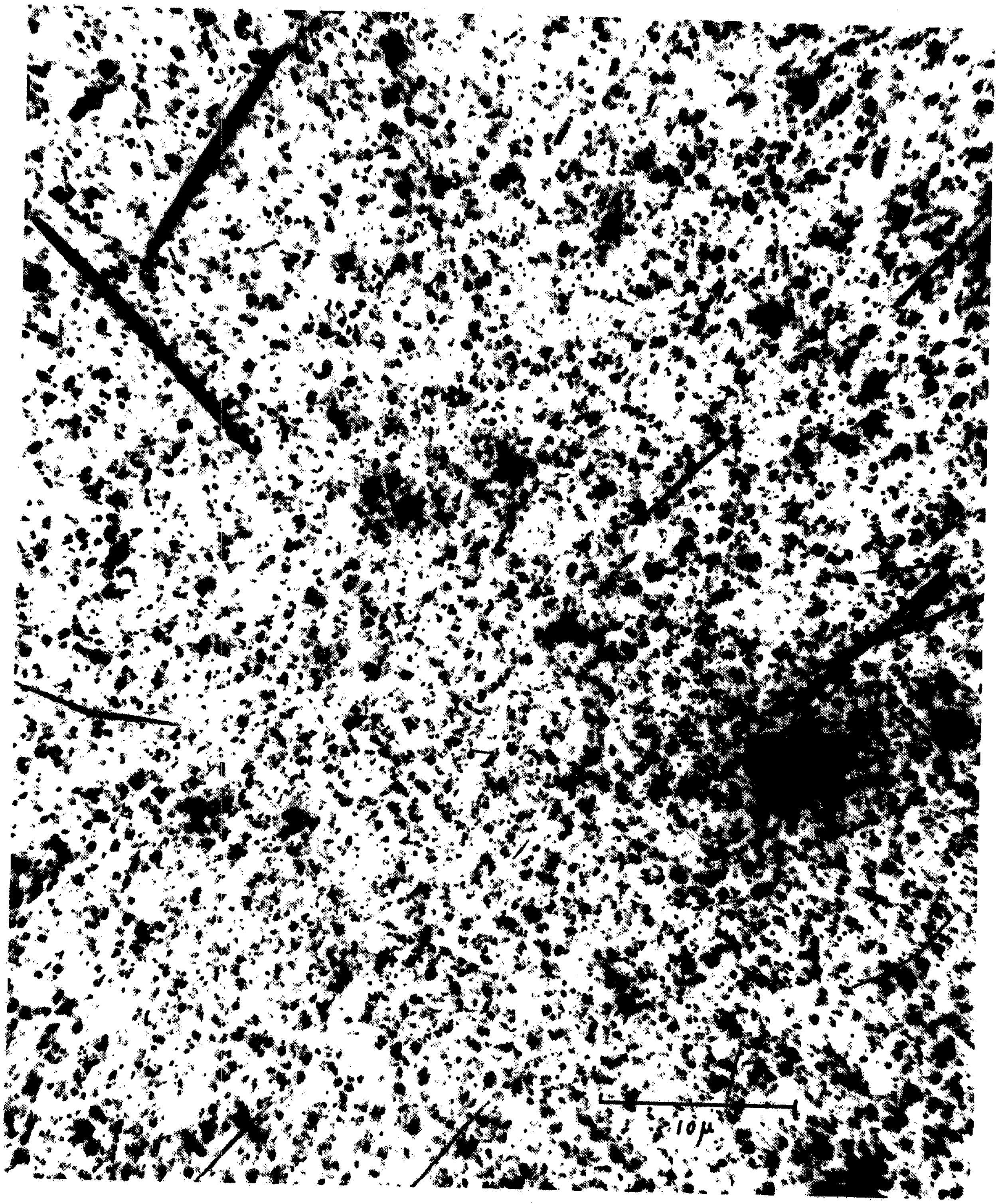

Plate 1202

3,500 X

Figure 5. Acid Pasted LB Masstone Lacquer

Aged 6 Months at 50°C

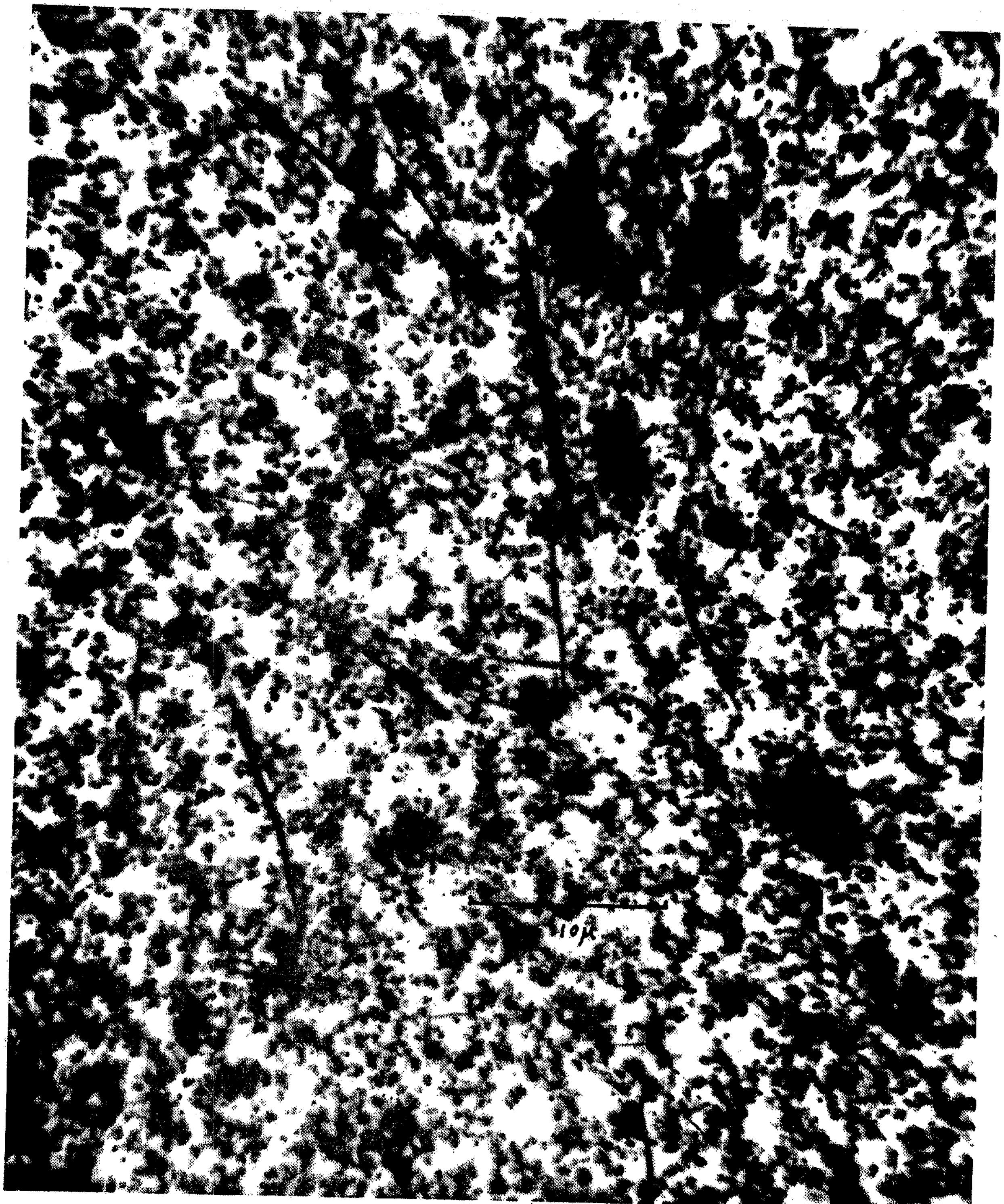

Plate 1340

3,500 X

Figure 6. Acid Pasted LB Masstone Lacquer

Aged 1 Year at 50°C

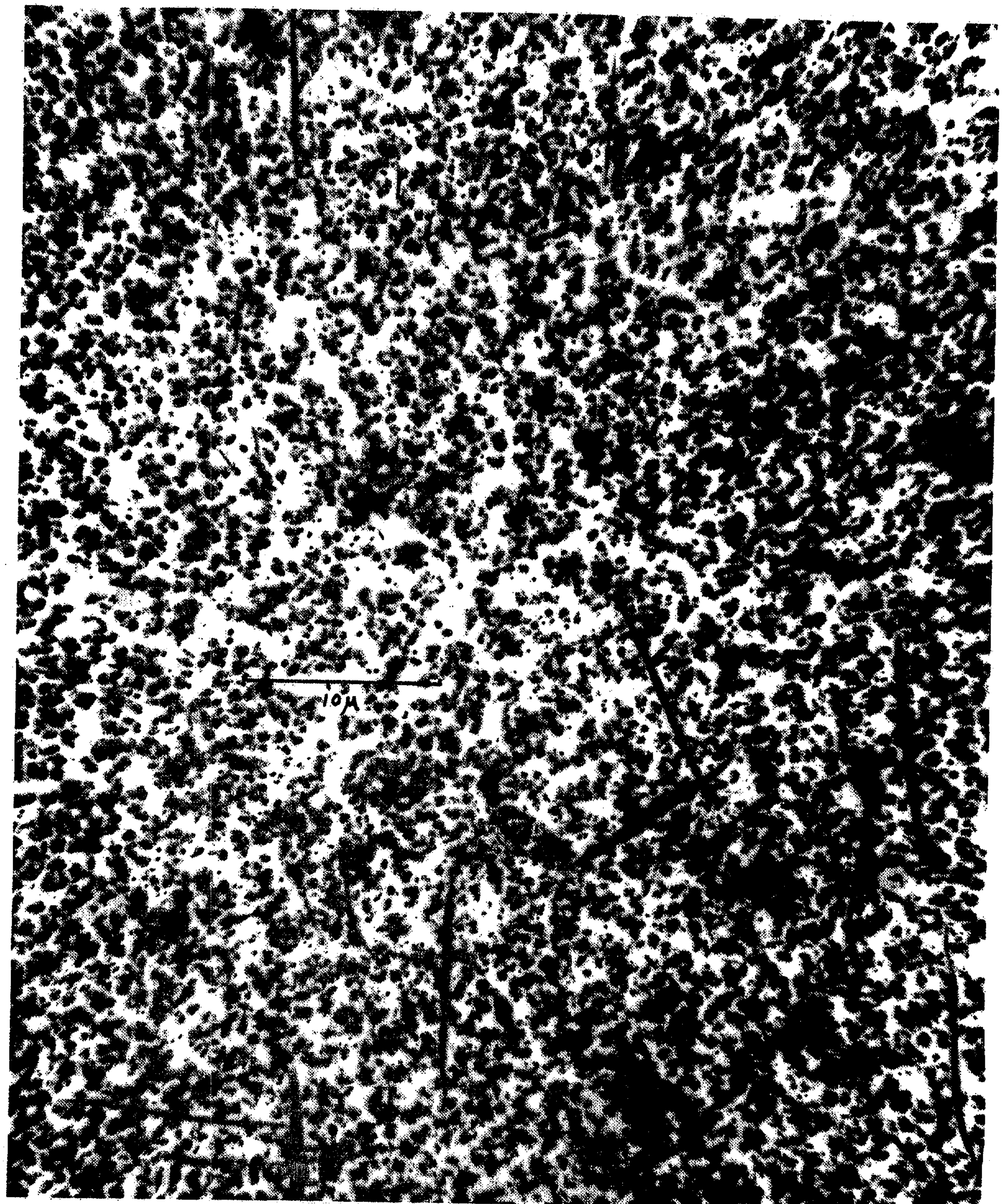

Plate 1424

3,500 X

Figure 7. Initial Acid Pasted Semi-chlor Masstone Lacquer

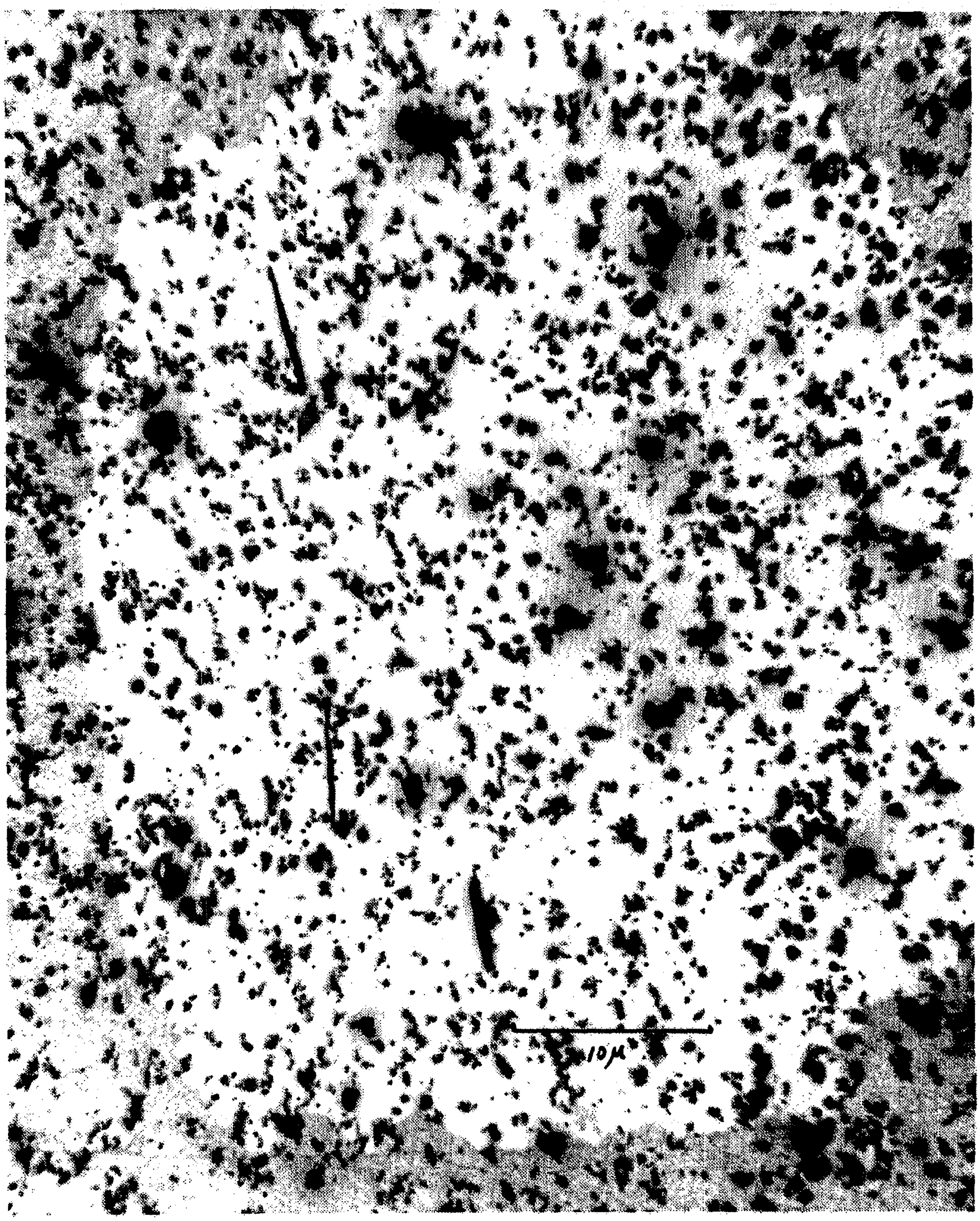

Plate 1188

3,500 X

Figure 8. Acid Pasted Semi-chlor Masstone Lacquer

Aged 1 Week at 50°C

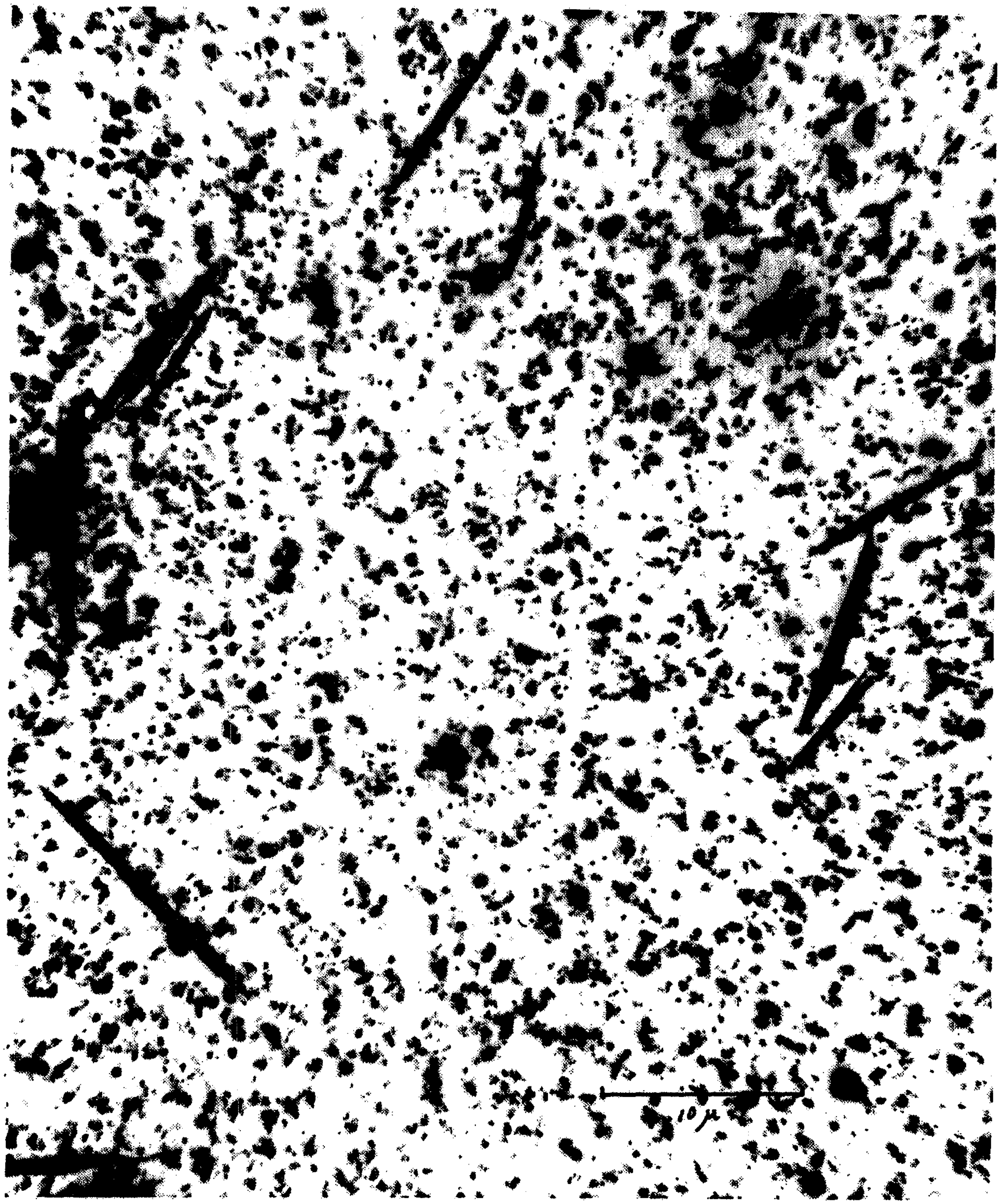

Plate 1193 3,500 X

DUP050068919

Figure 9. Acid Pasted Semi-chlor Masstone Lacquer
Aged 5 Weeks at 50°C

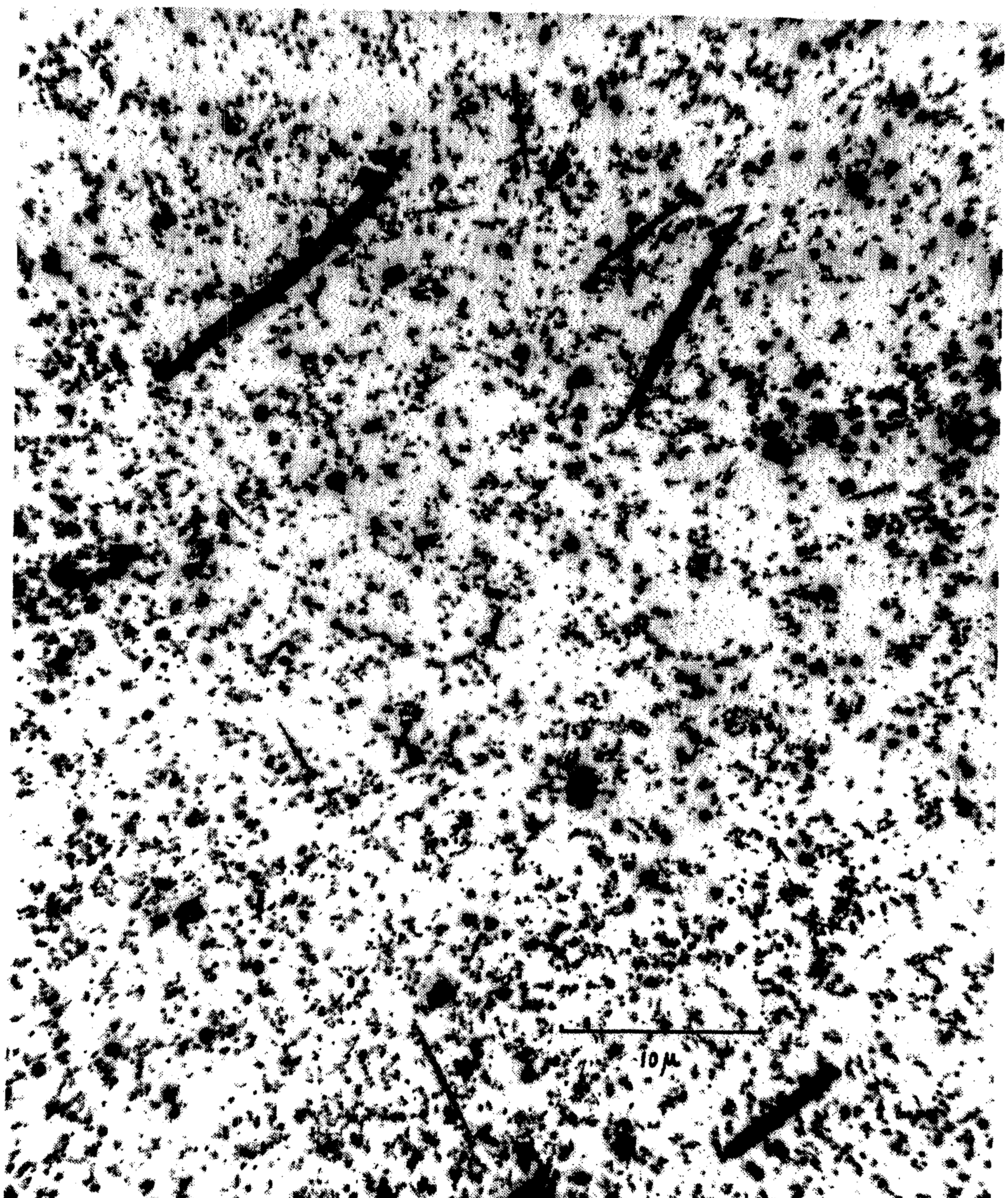

Plate 1201 3,500 X

Figure 10. Acid Pasted Semi-chlor Masstone

Lacquer Aged 6 Months at 50°C

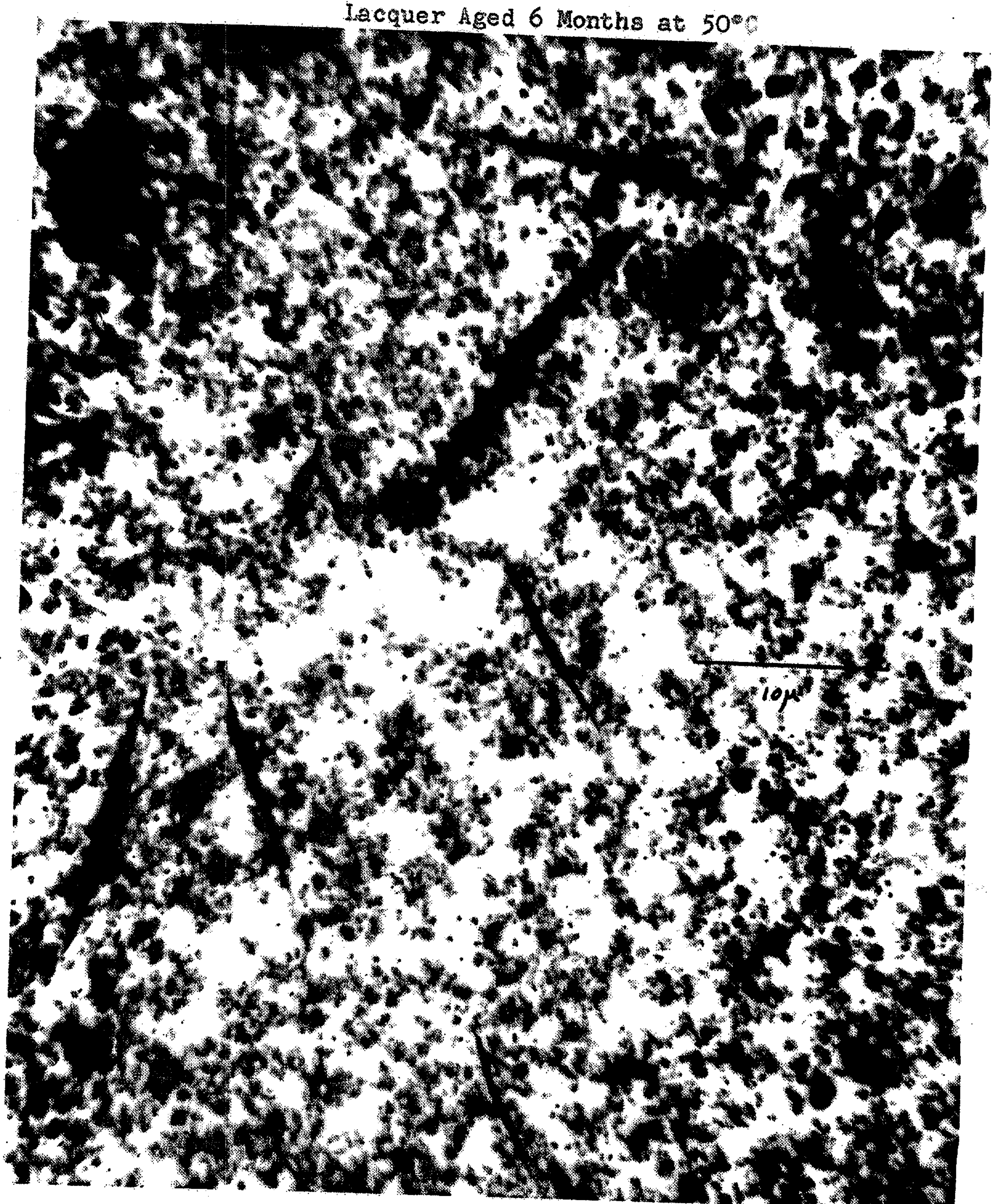

Plate 1339

3,500 X

Figure 11. Acid Pasted Semi-chlor Masstone Lacquer

Aged 1 Year at 50°C

Plate 1423

3,500 X