Serial No. KN-69-8

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

PREPARATION OF PIGMENTARY QUINACRIDONE BY VACUUM SUBLIMATION FOLLOWED BY SOLVENT ACTION

Period Covered August, 1962 to March, 1968 (Part time)

FILE: 223.91

DATE: 7/8/69

NJ 14071

KM-68-8 PREPARATION OF PIGMENTARY QUINACRIDONE BY VACUUM SUBLIMATION FOLLOWED BY SOLVENT ACTION By: A. P

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

SUBJECT: PREPARATION OF PIGMENTARY QUINACRIDONE BY VACUUM SUBLIMATION FOLLOWED BY SOLVENT ACTION.

PERIOD COVERED: Part time from August, 1962 to March, 1968

SUBMITTED BY: A. R. HANKE
A R Hanke

Date Submitted: 7/3/69
Date Released: 7/8/69

ABSTRACT

Pigmentary α, β, and γ phase quinacridone can be obtained by solvent treating (breaching) vacuum sublimed quinacridone.

Vacuum heating α phase quinacridone causes phase changes to β and γ but the changes are not clear cut and it will be difficult to obtain a pure phase species of pigmentary crystallite size by this method.

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OBJECTIVE

This work was undertaken to determine if pigmentary quinacridones could be obtained via a vacuum evaporation finishing step.

SUMMARY AND CONCLUSION

1. It is possible to solvent treat vacuum sublimed and condensed QA and obtain at one's option, pigmentary α, β, or γ phases.

2. When QA is vacuum sublimed and condensed on a room temperature surface, the product is poorly crystalline. The X-ray record gives no indication of γ phase. There is some indication of α phase and another unidentified phase that bears some resemblance to β.

3. By varnish drier rubout, the extension is weak and its hue would suggest a mixture of the violet β phase and red α phase but as mentioned in (2), the X-ray record does not give clear-cut evidence of βQA.

4. This poorly crystalline condensate is highly sensitive to phase conversion through solvent action and the phase that is produced depends on the solvent and the temperature.

5. Room temperature exposure of the vacuum sublimed QA to dimethylformamide (DMF) for 15 min. gives complete transformation to pigmentary γQA. The pigment so produced has more color strength, is yellower in hue, more intense, and lighter in masstone than RT-790-D, SD-82154.

6. Complete conversion of the vacuum sublimed QA to β phase occurs upon o-dichlorbenzene reflux for 15 min. The pigmentary β phase obtained in this manner is equal in color strength, bluer in hue, and lighter in masstone than RT-791-D, SD-97187.

7. Complete conversion of the vacuum sublimed QA to α phase occurs upon exposure to ODCB at 34°C. for around 256 hrs. It is possible that a more detailed study of the relationship between time and temperature could produce a more reasonable method for converting to α phase. The product has much more color strength, is bluer, in hue, more intense, and has a darker masstone than RT-790-D, SD-82154.

8. Vacuum heating αQA at temperatures close to sublimation temperatures for prolonged periods of time cause very slow conversion of α to highly crystalline β phase. No γ phase is formed until temperatures are reached that cause considerable pyrolysis. This suggests that it will be difficult to control the crystal phase and achieve pigmentary products by time and temperature control alone.

EXPERIMENTAL TECHNIQUE

A bell jar type vacuum evaporator was used in the range of 10^{-4}mm Hg for the sublimation experiments. The sample was a dispersion-milled γQA type similar to RT-798-P but containing no $NiCO_3$ or blanc fixe. Initial experiments used a platinum boat to contain the sample, but this technique was replaced with one using a small porcelain crucible with a platinum wire spiral in it. This allowed the use of a larger sample. In all cases, heating was achieved by passing a current through the platinum. The temperature was not monitored and different temperatures were obtained by simply changing the voltage on the platinum.

The subliming QA was allowed to condense on the walls of the bell jar. In addition to this, an aluminum holder designed to hold glass and quartz slides was used and deposits were made on such slides. This made it possible to obtain light transmittance curves and X-ray records of the condensate without disturbing it in any way. X-ray records were also obtained on material scraped from the walls of the bell jar. All diffraction patterns were derived from CuK_α radiation.

Since this material proved to be a mixture of crystal phases, it was subjected to the action of solvents dimethylformamide (DMF), o-dichlorbenzene (ODCB), α-Cl naphthalene, and Xylene. After solvent treatment, X-ray diffraction was used to assess any phase changes. Electron micrographs furnished information on crystallite size and shape.

In the attempt to use temperature as a crystal phase controller, the "Pt coil in a crucible" technique was used with a cover on the crucible to contain the sample. The sample was an αQA designated ASF 85, Lot 11030. Temperature was controlled by varying the voltage across the Pt coil. The temperature was not measured but relative values could be designated by the voltage measurements. Such relative temperatures were maintained for different time intervals.

RESULTS AND DISCUSSION

A. Vacuum Evaporation

Fig. 1 shows an X-ray record of material condensed on the walls of the bell jar. Superimposed on the patterns are short vertical lines indicating the positions of the α, β, and γ phase quinacridone X-ray diffraction peaks. In addition, there are three broad peaks labeled with question marks. These peaks are at 11.4°, 15.1°, and 22.9° 2θ and do not line up with either α, β, or γ phases. Due to the low degree of crystallinity, it is difficult to determine just what phases are present in this vacuum evaporated material. It is unlikely that much, if any, γ phase is present because there is no indication of a peak at 13.1°. Also, no peaks are evident at 23.7° and 26.3°. A better case can be made for α phase. The peaks at 12.5°, 14.1°, 25.9° are indicative of α phase.

The possible presence of β phase is difficult to assess. There are peaks close enough to 5.9°, 11.8°, and 27.1° to suggest β but nothing at 16° or 22° unless one considers the peaks marked with a question mark. These are too far removed and suggest the presence of another crystal phase. It is conceivable that this is a modified β phase.

A light transmittance curve of the condensate on a quartz slide yields the following information along with that of typical dispersions of α, β, and γQA.

	max (nm)
Vacuum evaporated condensate	523 and 560
αQA dispersion	520 and 556
βQA dispersion	525 and 577
γQA dispersion	521 and 556

Spectrophotometric measurements do not distinguish between α, and γQA, but since α phase is suggested by X-ray diffraction, the results can be interpreted as indicating a mixture of α phase and β phase or at least, something resembling the tinctorial properties of β phase. The appearance of a varnish drier rubout leads to the same conclusion.

Fig. 2 is an electron micrograph of the condensate. It shows small, non-crystalline appearing particles along with larger (1.5μ) aggregates. These aggregates represent "unbreached" particles that can be breached by solvent action. A varnish drier rubout shows the product to be dull, weak, and about midway in blueness between γ and βQA, RT-790-D, and RT-791-D.

B. Effect of Solvents on Vacuum Evaporated QA

The action of solvents on vacuum evaporated QA is twofold. First, there is the "breaching effect" that causes the large aggregates to disintegrate into small crystals and secondly, there is a crystal phase change. The particular phase that is favored depends on the nature of the solvent. For example, a 15 min. room temperature soak in dimethylformamide (DMF) leads to the lowest energy level pigmentary γ phase. Refluxing in less polar solvents such as Xylene, o-dichlorbenzene (ODCB) or α-chlornaphalene leads to the intermediate energy level β phase. For example, refluxing in ODCB for 15 min. yields pigmentary β phase. A milder treatment with a less polar solvent leads to α phase. For example, treatment with ODCB at 34°C. for 256 hrs. yields pigmentary α phase.

It is true that the energy level for the three crystal phases depends on the crystallite size and because of this size dependence, the energy level of one phase can overlap into the energy level range of an adjacent phase. This has been pointed out by C. W. Manger in KN-56-2. But, it is believed that at comparable crystallite sizes, the energy levels go from α to β to γ in decreasing order. If this is true, the vacuum evaporated material must

represent a higher degree of disorder (higher energy) than crystalline α phase because it can be converted to α phase by solvent action. This means that the non-α phase portion of the vacuum evaporated QA is either a type of β phase that has a higher energy level than typical α phase or a new phase is present that exists at a higher energy level than the α phase.

Fig. 3 is an X-ray record of vacuum sublimed QA exposed to room temperature DMF for 15 min. It is that of a typical pigmentary γ phase QA.

Fig. 4 is an electron micrograph of the same material. By varnish drier rubout, it is stronger, yellower, and more intense than the γ phase QA RT-790-D, SD-82154. It is also lighter in masstone.

Fig. 5 is an X-ray record of vacuum evaporated QA refluxed for 15 min. in ODCB. It is that of a typical pigmentary β phase QA.

Fig. 6 is an electron micrograph of the same sample. By rubout, it is equal in color strength, bluer in hue, and lighter in masstone than the β phase QA RT-791-D, SD-97189.

Fig. 7 is an X-ray record of vacuum sublimed QA stirred in ODCB at 34°C. for 256 hrs. It is that of a typical pigmentary αQA.

Fig. 8 is an electron micrograph of the same material. By varnish drier rubout, it is much stronger, bluer, and more intense than the γ phase QA RT-790-D. It is also darker in masstone.

The electron micrographs of both γ and β phases (Fig. 4 and 6) show crystal sizes larger than the corresponding RT-790-D and RT-791-D. They both appear thin and there is a greater tendency towards acicularity with the γ phase than with the β phase. This habit tendency is also observed in the RT-790-D and RT-791-D standards.

It is to be noted that in spite of the fact that the crystals appear larger in the vacuum evaporated, solvent-treated products than with the corresponding standard pigments, the color strength is comparable. This can be explained by realizing that in this size range, the rate of change of color strength with respect to particle size is small. This observation comes from the application of the Mie theory which describes the relationship between particle size and light absorption and scattering. Also, the plate-like habit of these pigments will allow crystal growth with but little change in their thin dimension. A growing crystal that maintains a constant thin dimension will not cause as much color strength loss as a crystal growing equally in all directions. The lighter masstone is associated with the larger crystallite size.

The electron micrograph of α phase (Fig. 8) shows crystals smaller than those of a typical pigmentary γQA and it is this small size that is responsible for the dark masstone.

VACUUM HEATING OF QA FOR CRYSTAL PHASE CONTROL

For this work, αQA was used as the starting material because it represents a high energy level crystal phase. Previous experience has shown that high temperatures can convert high energy crystal phases to lower energy ones by supplying sufficient thermal energy to overcome an energy barrier. This sample was prepared in the Semi-Works by acid swelling QA in 70% sulfuric acid and drowning into water. The product is designated ASF-85, Lot 11030.

During vacuum heating, the temperature was not monitored but could be varied by varying the voltage across the platinum coil. Some idea of the temperature range can be had from earlier work where hot stage X-ray diffraction showed no phase change until temperatures in excess of 350°C. were reached (NB 1657-7).

The results of all vacuum heating experiments are summarized in the following table.

Voltage	Time	Results
18	20 min.	Highly crystalline β and γ. No α. Considerable decomposition.
16	20 min.	Mostly β. Some γ. All highly crystalline. No α. Considerable decomposition.
14	1-1/2 hr.	Mostly β. Very little, if any, γ. Some initial α. All highly crystalline. Considerable decomposition.
10	15 min.	Mostly initial α. Small amount of β. No γ. Very little, if any, decomposition.
10	10-1/2 hr.	Mostly β. Some α. All highly crystalline. No γ. Very little, if any, decomposition.
10	29-1/2 hr.	This is a continuation of the 10-1/2 hr. sample. More β than at 10-1/2 hrs. Less α. All highly crystalline. No γ. Very little, if any, decomposition.

Certain generalizations can be drawn from these results. At the temperature reached by 14 to 18 volts, there is considerable decomposition even in a vacuum. The product one gets by heating under these conditions is always a mixture of crystal phases. There is some evidence that prolonged low temperature (10 volts) heating would give all β phase but excessive time would be required. The higher temperatures favor γ phase. All heating tends to increase the degree of crystallinity and even moderate heating will lead to highly crystalline products.

These observations suggest that it will be difficult to obtain a single crystal phase species using heat alone as a means of phase control.

PATENT SITUATION

It is planned to submit a patent application covering this work.

NOTEBOOK RECORD

1737-5 (1962)

QA was vacuum sublimed with the intent of examining the tinctorial properties.

1882-23, 24 (1968)

QA was vacuum sublimed and the sublimate subjected to solvent action.

1882-26 (1968)

QA was vacuum heated at different temperatures and phase changes observed.

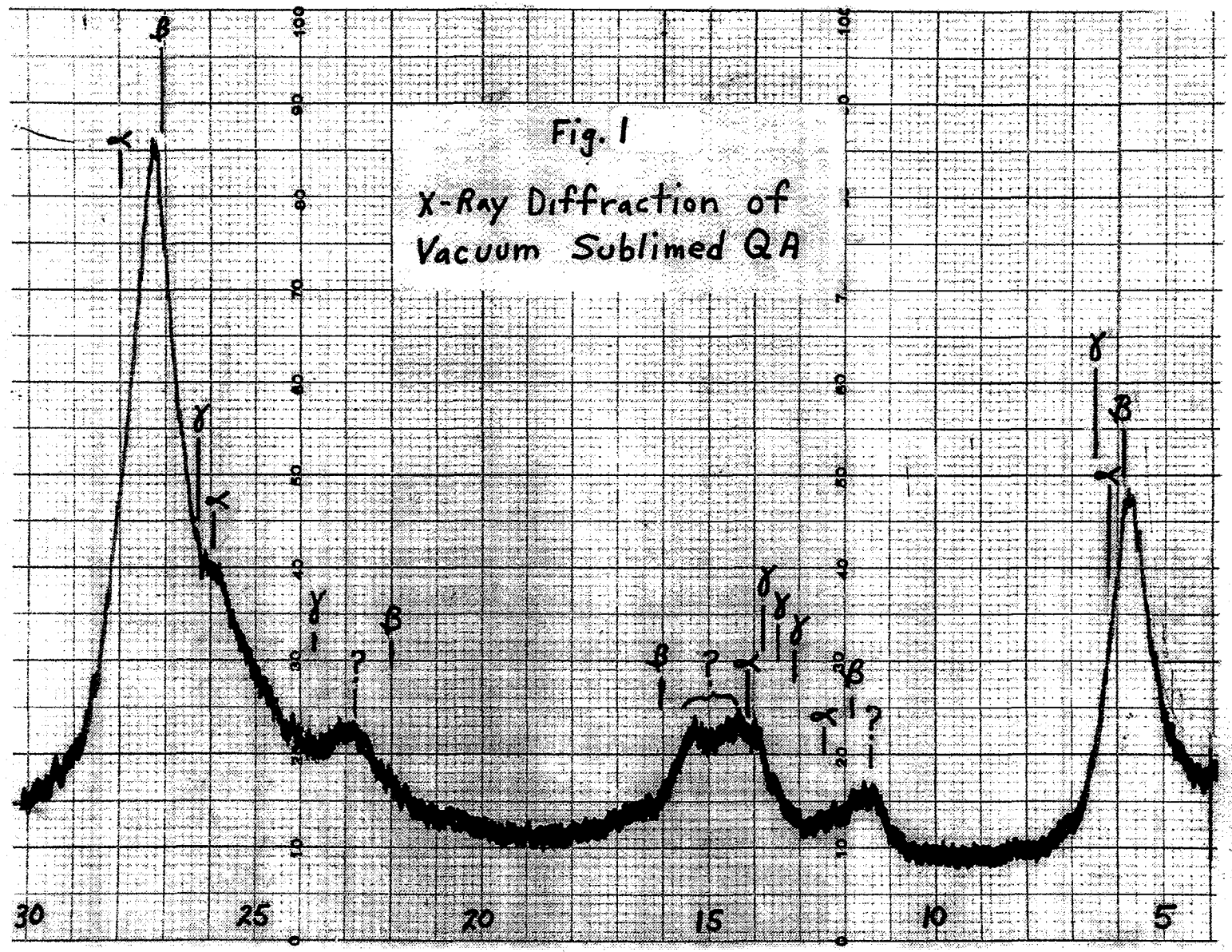
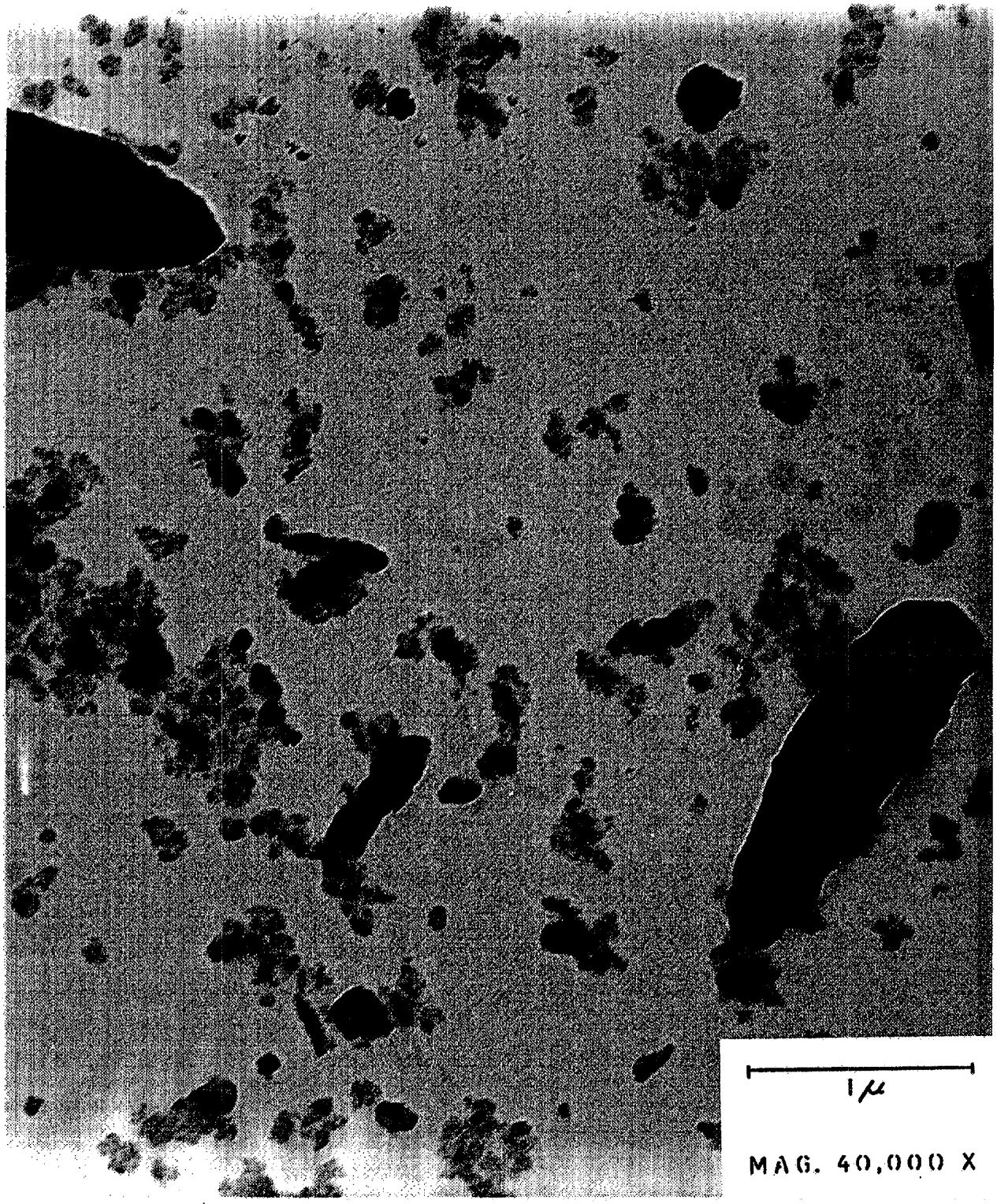


Fig. 2

Vacuum Sublimed QA



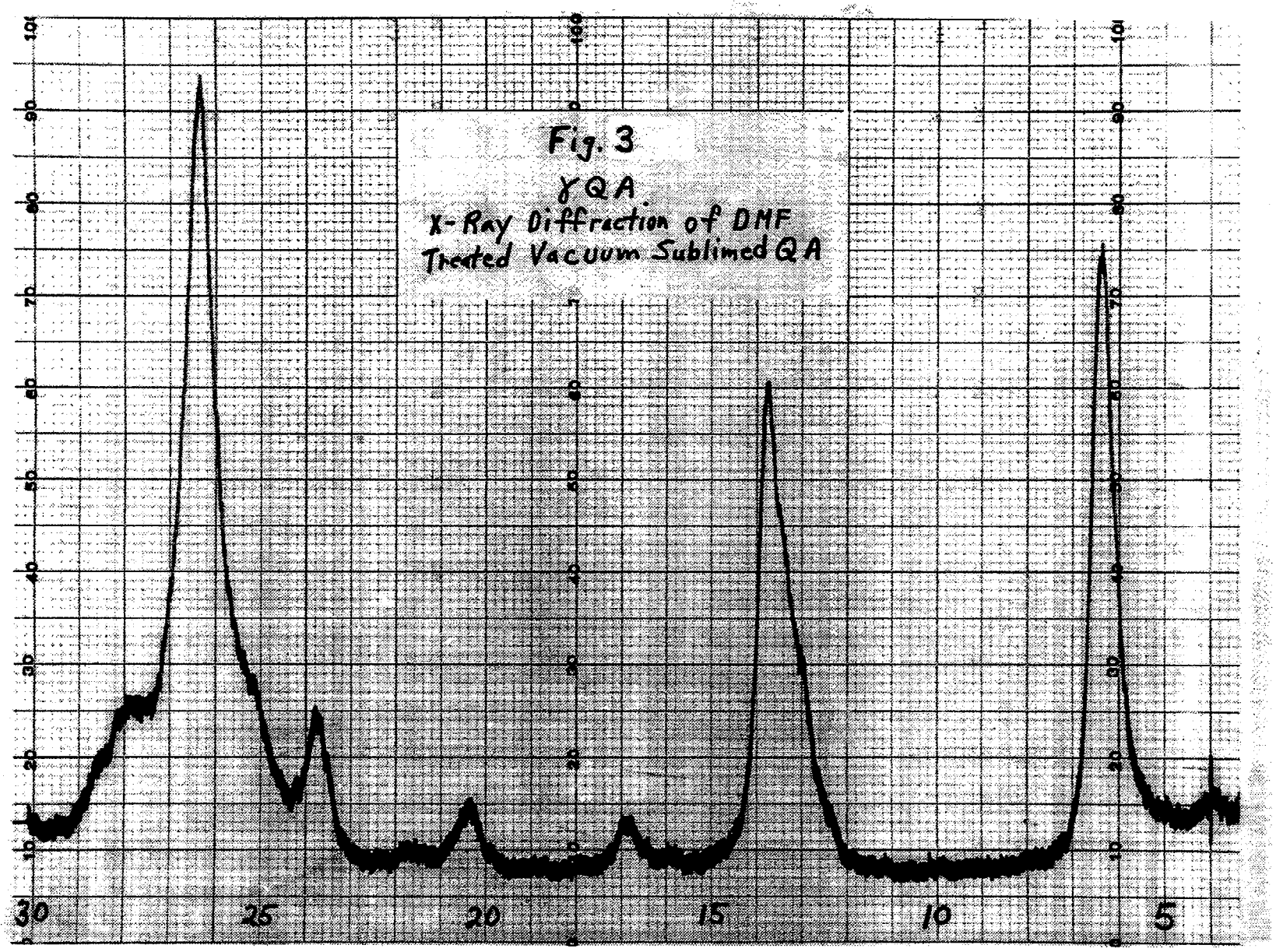
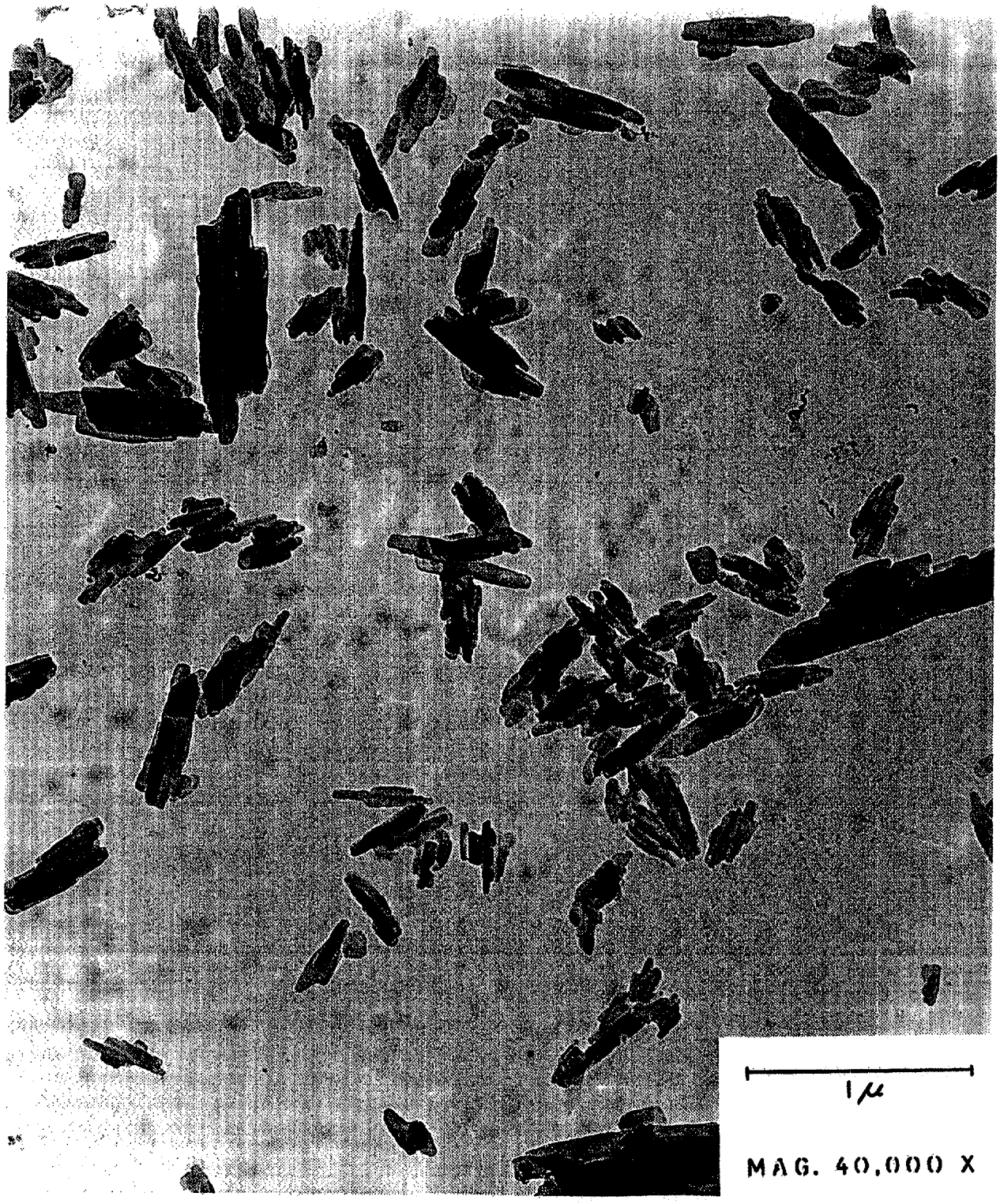


Fig. 4

Vacuum Sublimed QA
Exposed to DMF
Pigmentary γQA



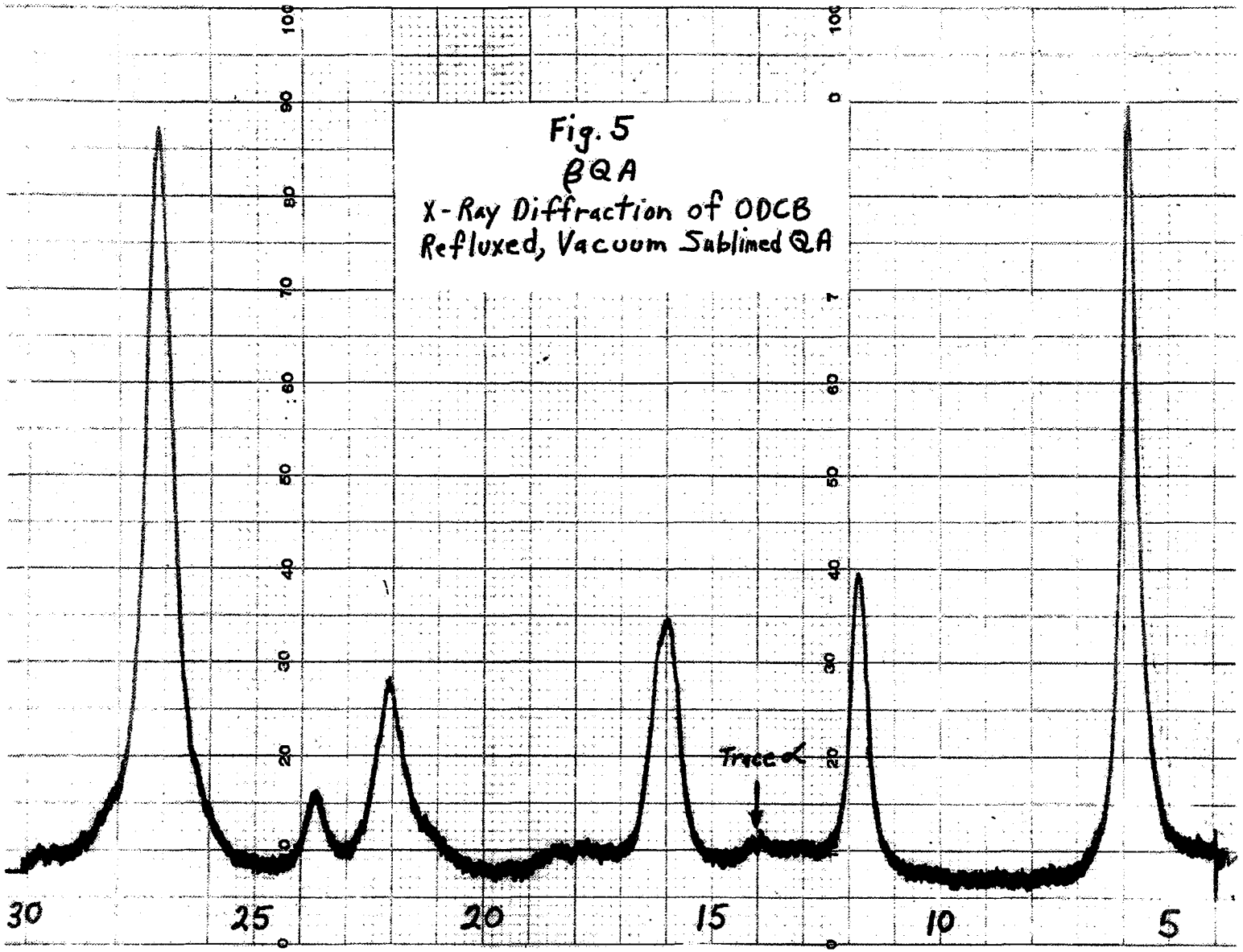
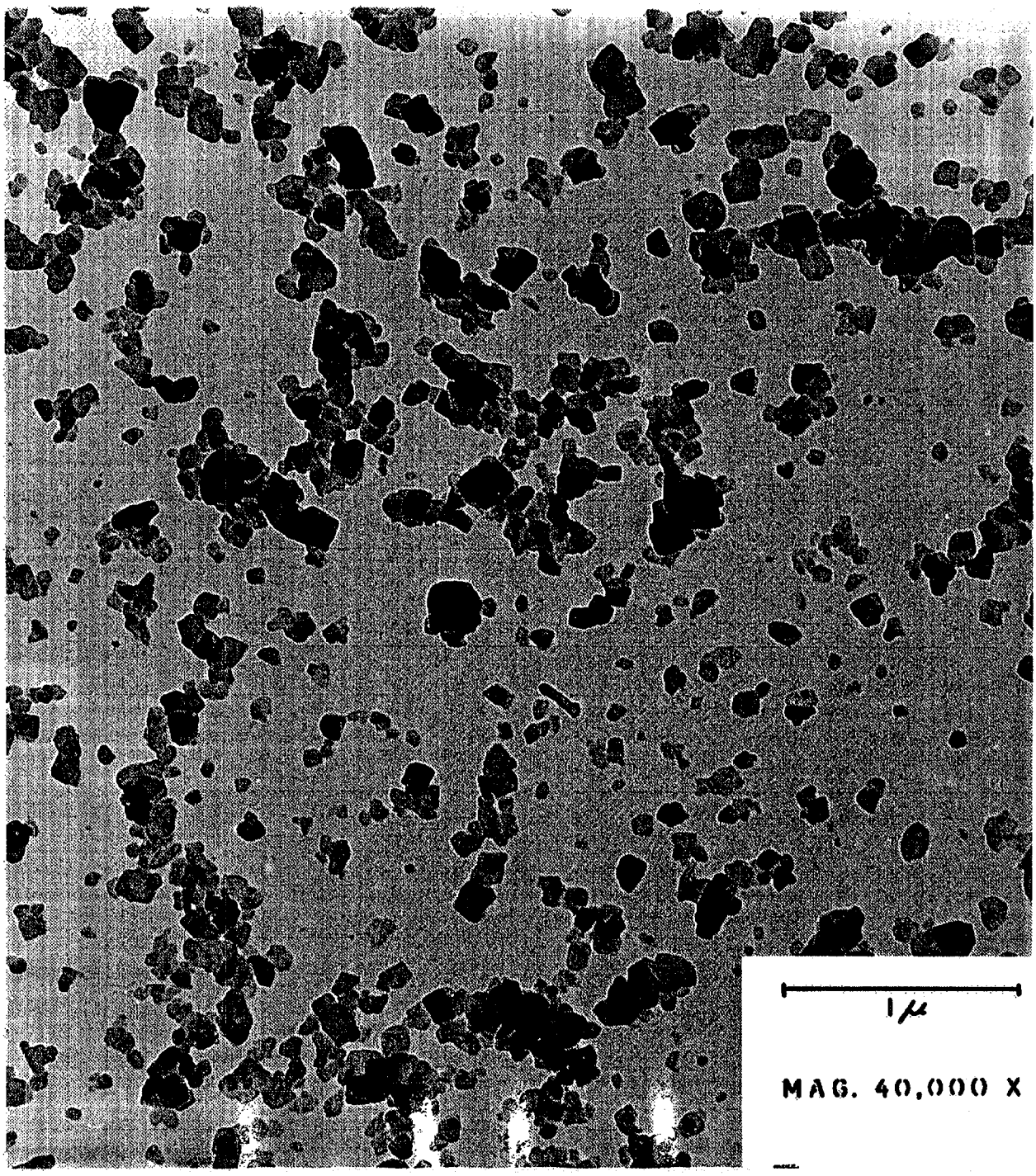


Fig. 6

Vacumm Sublimed QA
Refluxed in ODCB
Pigmentary βQA



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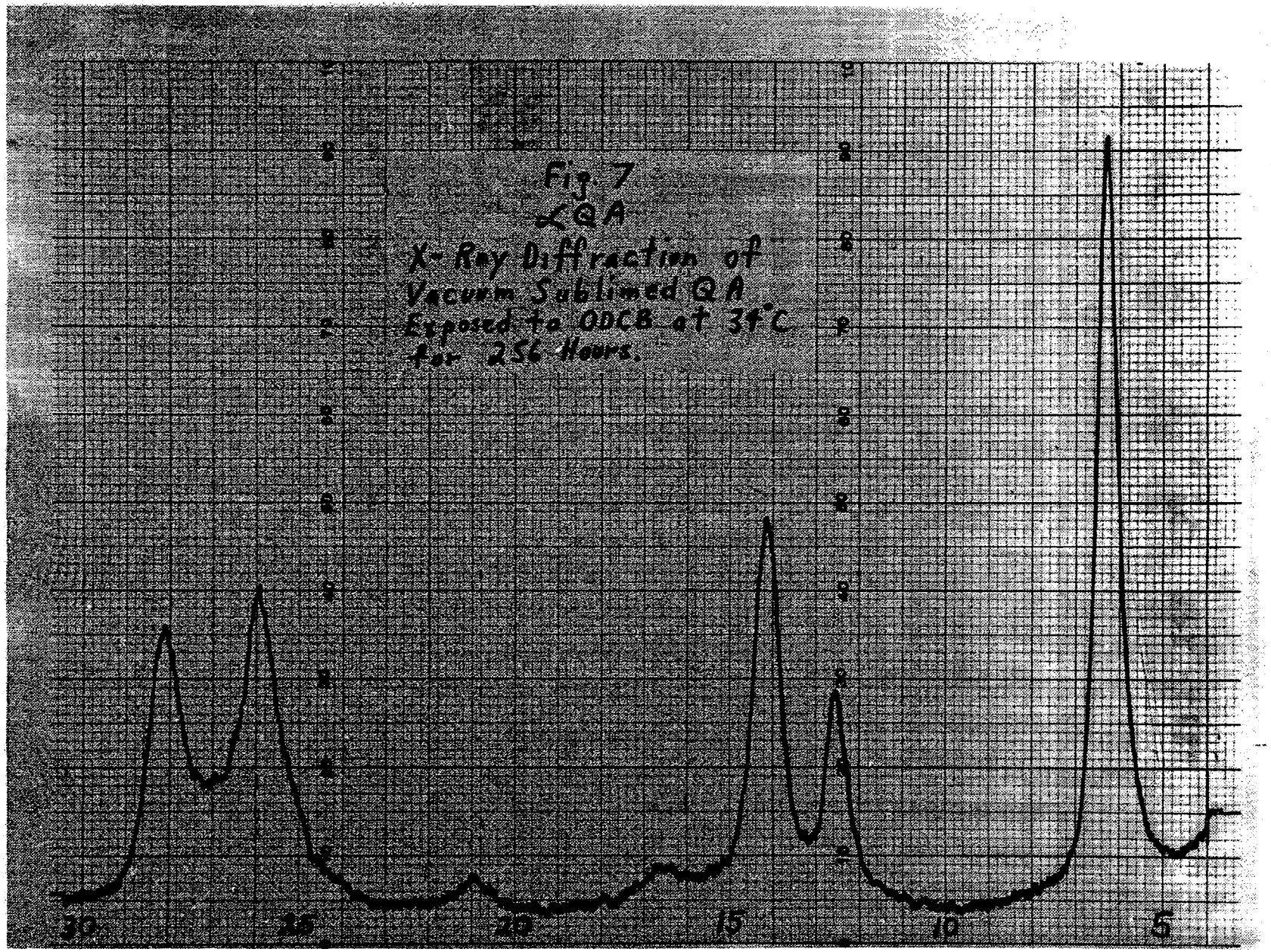

Fig. 7
∠QA
X-Ray Diffraction of
Vacuum Sublimed QA
Exposed to ODCB at 31°C
for 256 Hours.

Fig. 8

Vacuum Sublimed QA
Exposed to ODCB at 34°C. for 256 hrs.
Pigmentary αQA