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PIGMENT COLOR RESEARCH REPORT

2,9-DIMETHYLQUINACRIDONE/QUINACRIDONE SOLID SOLUTIONS:
CHARACTERIZATION

Period Covered July, 1967 - September, 1967

FILE: 223.91

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NEWARK PLANT

PIGMENT COLORS RESEARCH REPORT

SUBJECT: 2,9-DIMETHYLQUINACRIDONE/QUINACRIDONE SOLID SOLUTIONS: CHARACTERIZATION

Period Covered: July, 1967 to September, 1967

Submitted by: C. W. Manger Date Submitted: 9/22/67

Approved by: B. H. PERKINS Date Released: 10/9/67

ABSTRACT:
A study was made to determine the differences between solid solutions of QA/2,9-dimethylQA and 2,9-dimethylQA, alone and in mixtures with QA.

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I. INTRODUCTION

Because of a patent situation with 2,9-dimethylquinacridone (2,9-dimethylQA), a brief study was made to determine the differences between solid solutions of 2,9-dimethylQA/QA and dry mix counterparts at low percentages of QA. The study was then expanded to include the complete range of composition from 0 to 100% 2,9-dimethylQA in QA.

II. SUMMARY AND CONCLUSIONS

1. Infrared spectra of solid solutions of QA in 2,9-dimethyl QA are subtly but distinctly different from those of dry mix counterparts in the range below ca. 20% QA.

2. The infrared band of QA in the 13 to 14 micron region varies in wavelength with the crystallographic phase (α, β, and γ) and with composition in solid solutions with 2,9-dimethylQA. A distinct difference in this band is evident between dry mixes and solid solutions (made by HT drowning or dimethylformamide reflux).

3. As little as 1% QA can be readily detected by infrared in mixtures with 2,9-dimethylQA as solid solutions or dry mixes (at ca. 13.35 microns).

4. It has not been possible to distinguish by x-ray diffraction between 100% β-2,9-dimethylQA and samples containing up to ca. 10-15% QA as a dry mix or solid solution.

5. In HT-drowned solid solutions, there is a definite change in x-ray diffraction peak positions with composition. Peaks due to the two largest interplanar spacings are essentially constant over the range 0 to 30% QA.

6. Flushout tints of solid solutions containing 10 and 20% QA are essentially equal to that of 2,9-dimethylQA. A definite cost advantage as well as patent coverage are suggested by this observation, since QA is less costly than 2,9-dimethylQA and solid solutions are covered by our existing patents.

III. PATENT SITUATION

This study was initiated because of the somewhat confusing patent situation involving 2,9-dimethylQA. It appears that it would be desirable if we would explore the possibilities of making and selling a tinctorially desirable product as a solid solution with low percentages of QA, e,g., 1 to 20%. This type of product would be covered by our solid solution patents.

IV. SUGGESTIONS FOR FURTHER WORK

In other present or future patent situations which concern substituted QA's, it may be possible to prepare solid solutions of the substituted QA's with low percentages of QA to give tinctorial properties essentially equal to those of the substituted QA itself.

V. EXPERIMENTAL DETAILS NB-1868-13,15

A. Samples Used

1. Available from Others

A considerable number of samples made by O.J.C. Klein by HT drowning was used in this study. These included the following:

Sample	Description
1794-17A	α-QA (undeveloped)
1794-17D	α-QA (developed)
1864-8A	β-2,9-dimethylQA
1864-8B	3%/97% QA/2,9-dimethylQA
1864-8C	6%/94% " "
1864-1A	7.5%/92.5% " "
1864-8D	12%/88% QA/2,9-dimethylQA
1846-44A	15%/85% " "
1846-9A	35%/65% " "
1846-32C	65%/35% " "

Samples available from the plant or others included:

1868-13A (CWM) HT-drowned β-QA toner (dried RT-887-D,lot 46303)
1713-7 (EEJ) Acid-crystallized α-QA
RT-796-D, PS-82148, Dispersion-milled γ-QA (10% Ni carbonate)
RT-849-D, TS-84232, Dispersion-milled Maroon B (40% dimethyl QA/60% QA + 10% Al hydrate)

2. Samples Prepared for this Study

a. Dry Mixes (1868-13)

The following dry mixes were made for a study of infrared spectra:

1868-13	B	C	D	E
% QA	10	10	10	1
Phase QA	α	β	γ	γ
QA Used	1794-17A	1868-13A	RT-796-D	RT-796-D
2,9-dimethylQA	1864-8A	8A	8A	8A

b. Refluxed Dry Mixes (1868-13)

The above mixes were refluxed in dimethylformamide for 4 hours to form solid solutions.

c. HT-Drowned Ladder Series (1868-15)

A 2,9-dimethylQA/QA ladder series from 0 to 100% 2,9-dimethylQA in 10% steps was made by HT drowning the appropriate mixtures of 98% sulfuric acid solutions according to

OJCK's currently preferred procedure for making "Maroon B" (35% 2,9-dimethylQA/65% QA) (1864-33A). This procedure used p-toluene sulfonic acid in the acid solution. The acid solution was drowned into water flowing at 16 liters/minute at 70°C. giving a Δ T of ca. 30°C. The slurry was boiled 90 minutes, treated with Emcol/Perclene emulsion, and then boiled to remove the Perclene. The samples were saved as presscakes (ca. 50 g. dry weight) except for a small quantity which was dried for analysis.

B. Results

1. Infrared Spectra

Mulls of the above samples in hexachlorobutadiene (HCB) show interesting differences in their infrared spectra in the region of 13 to 14 microns. (The ordinarily used Nujol has a weak band in this region).

Fortunately, 2,9-dimethylQA has no absorption band in this region where QA absorbs very strongly.

The position of the QA band(s) varies among the three phases of QA as shown in Figure 1. The band wavelength also varies with the composition of solid solutions of QA/2,9-dimethylQA made by HT drowning as shown in Figure 2.

Figure 3 shows the definite change in the QA band when dry mixes of 10% QA, as the α, β, or γ phase, with 90% β-2,9-dimethyl-QA are refluxed in dimethylformamide to form the solid solutions. Mixes from all three QA phases give the same solid solution on refluxing in DMF or on HT drowning.

Figure 3 also shows that as little as 1% QA can be readily detected by infrared.

Potential analytical infrared wavelengths and their approximate limits of detectability for QA and 2,9-dimethylQA in solid solutions of the two are as follows:

QA		2,9-DimethylQA	
Microns	%	Microns	%
9.74	10	8.32	10
10.40	10	10.92	10
13.35	1		

2. X-Ray Diffraction

Although the x-ray diffraction records of QA and 2,9-dimethylQA are quite different from each other, as shown in Figure 4, it has not been possible to distinguish by x-ray diffraction between 100% β-2,9-dimethylQA and samples containing up to ca. 10-15% QA as a dry mix or solid solution.

Figure 1

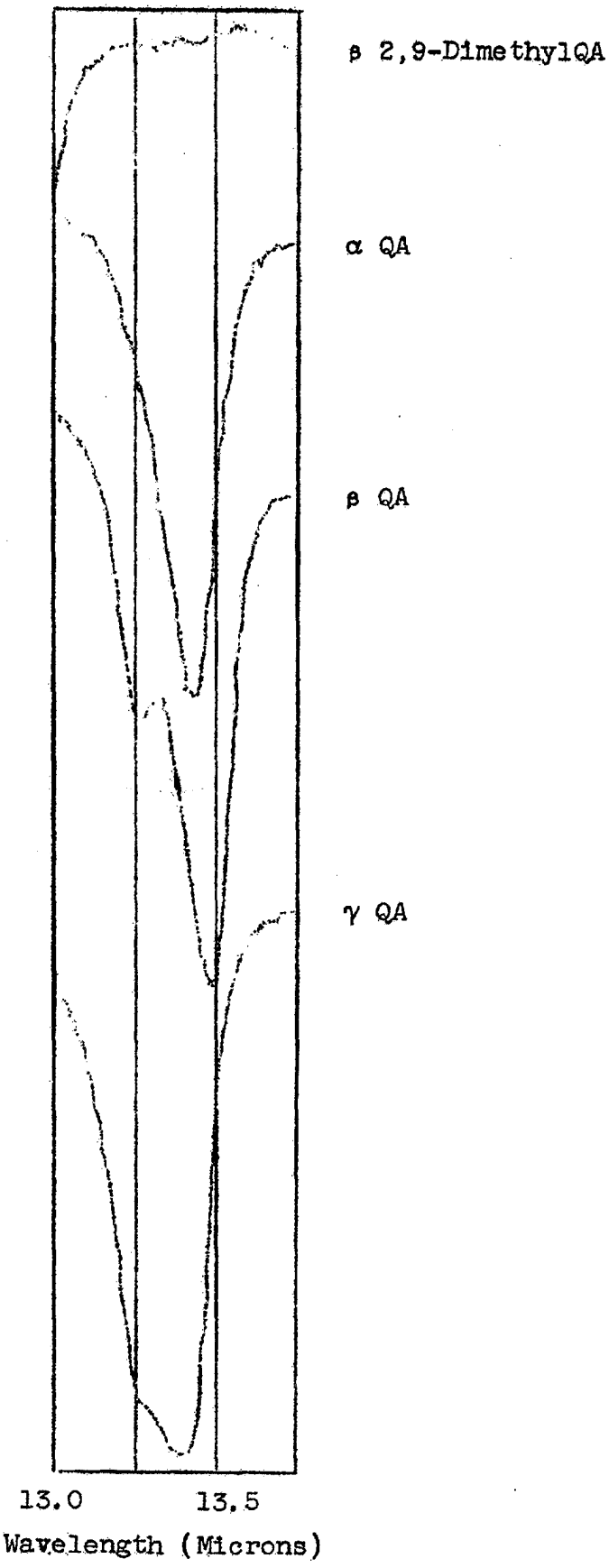
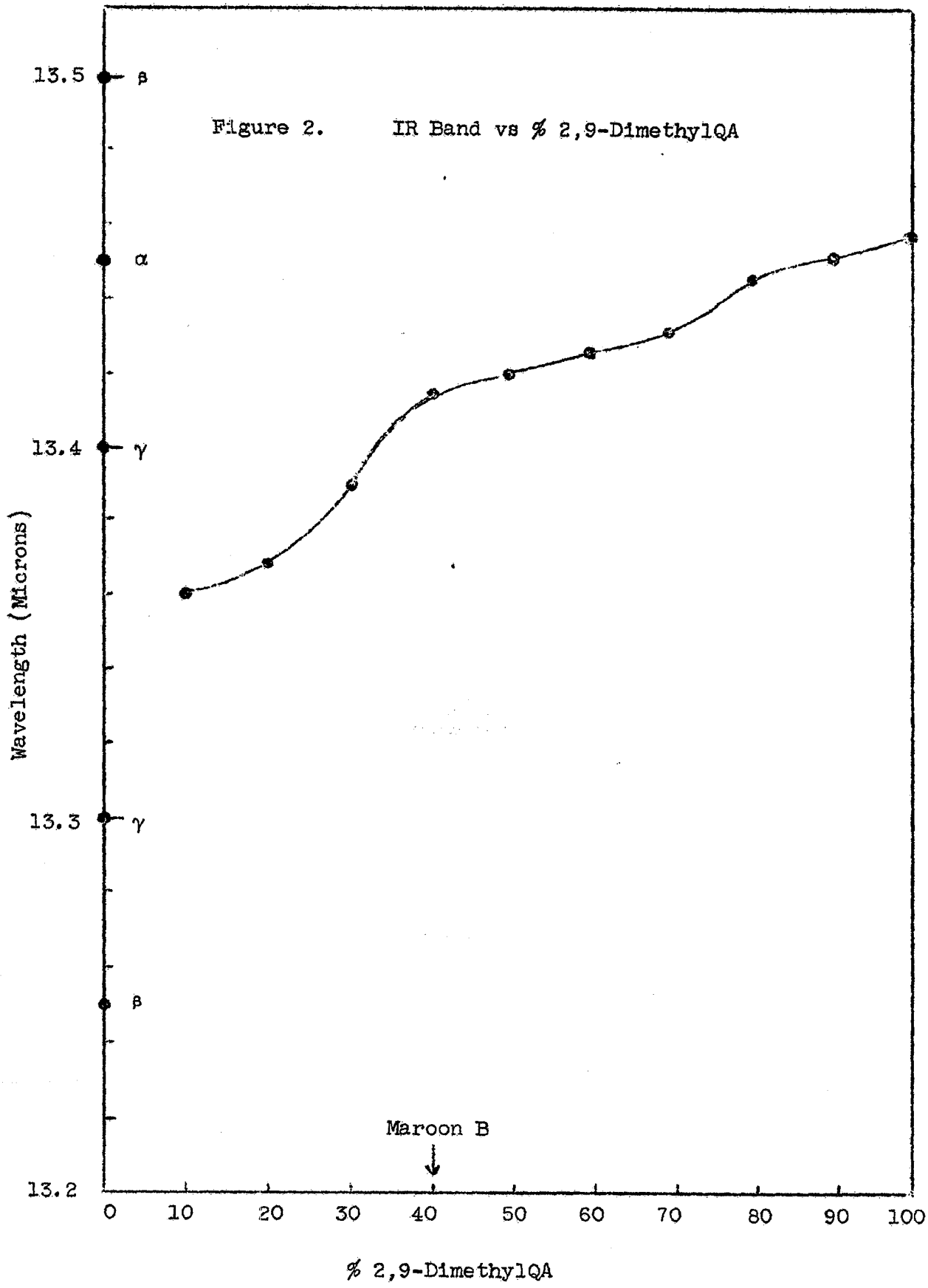


Figure 2. IR Band vs % 2,9-DimethylQA



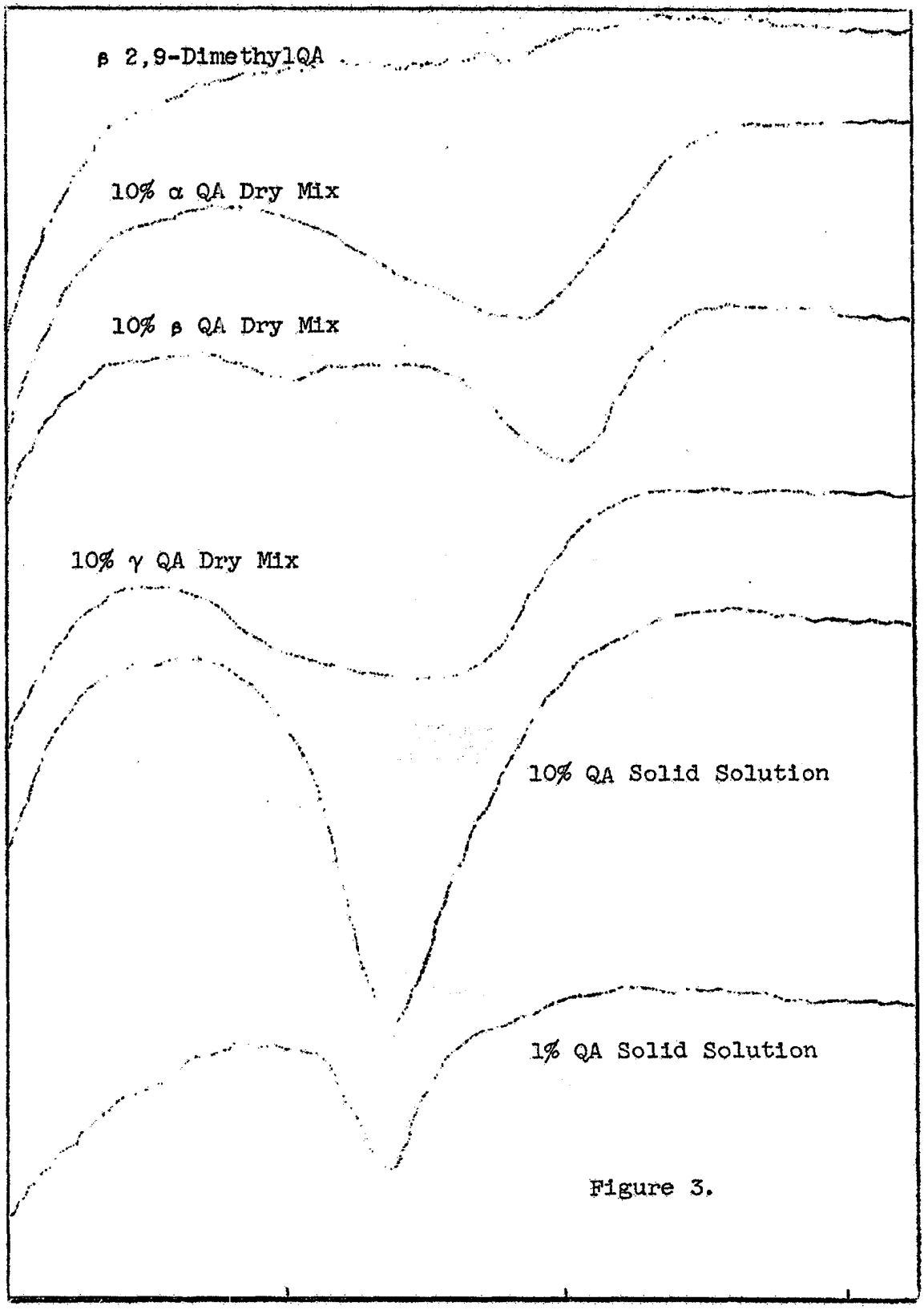


Figure 3.

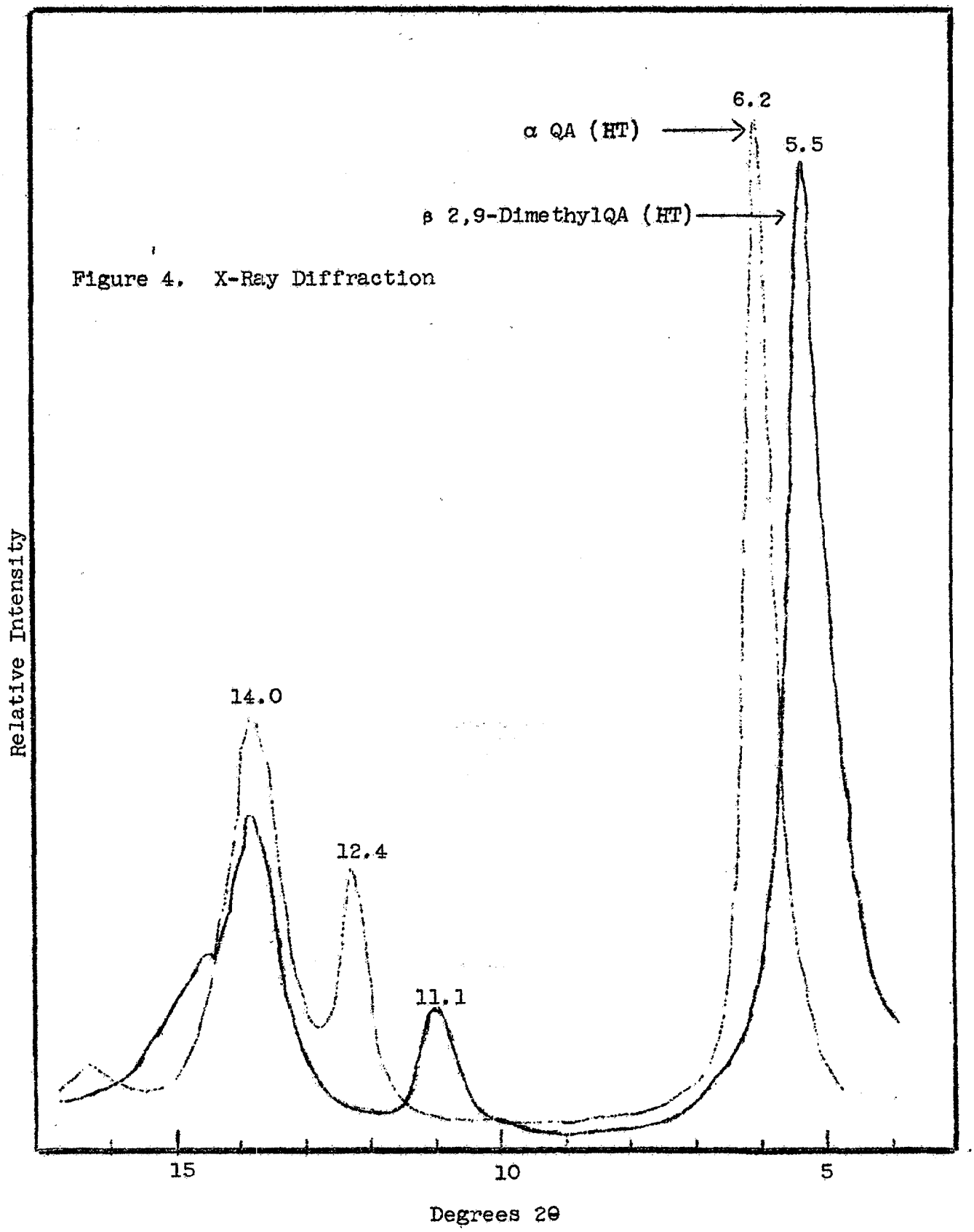


Figure 4. X-Ray Diffraction

Figures 5 and 6 show interesting changes in diffraction peak positions (degrees 2θ) with % 2,9-dimethylQA in solid solution with QA. It should be kept in mind that the peaks at ca. 11.0 to 12.4° are second order to those at ca. 5.4 to 6.2° and would vary proportionately. The peaks at 13.5 to 13.9° are not related to the above and may actually be unresolved multiple peaks.

3. Hue of Solid Solutions

Flushout tints of the QA/2,9-dimethylQA HT-drowned ladder series at the low % QA end show that the tint hue is surprisingly close among the samples 0, 10, and 20% QA. There is an abrupt change to a yellower hue at 30% versus 20% QA and 40% QA is definitely yellower vs. 30% QA.

As expected, mixes of 10 and 20% β-QA with 2,9-dimethylQA are progressively bluer in tint than the 2,9-dimethylQA. The tint of the 20% β-QA mix is considerably bluer vs. the solid solution counterpart.

Mixes of 10% and 20% γQA with 2,9-dimethylQA, as expected, are progressively yellower in tint than 2,9-dimethylQA. The 20% γQA is considerably yellower vs. the solid solution counterpart.

C. Procedure for Preparing Mulls for Infrared Spectrophotometry

The procedure used in this study for preparing mulls is as follows:

Weigh into stainless steel Wig-L-Bug capsule on rubout balance 0.600 g. Nujol, Hexachlorobutadiene (HCB), etc.

Add 0.200 g. sample by weighing into capsule or by weighing separately.

Add 6 - 1/8" steel shot.

Place cap on capsule and apply black electrical tape to avoid any leakage.

Place in Spex Mixer Mill holder using any or all of the six outer holes.

Place in Mixer Mill, clamping tightly.

Mill 20 minutes, using automatic timer.

Place portion of mull between rock salt plates.

Adjust amount of sample at desired wavelength and run spectrum.

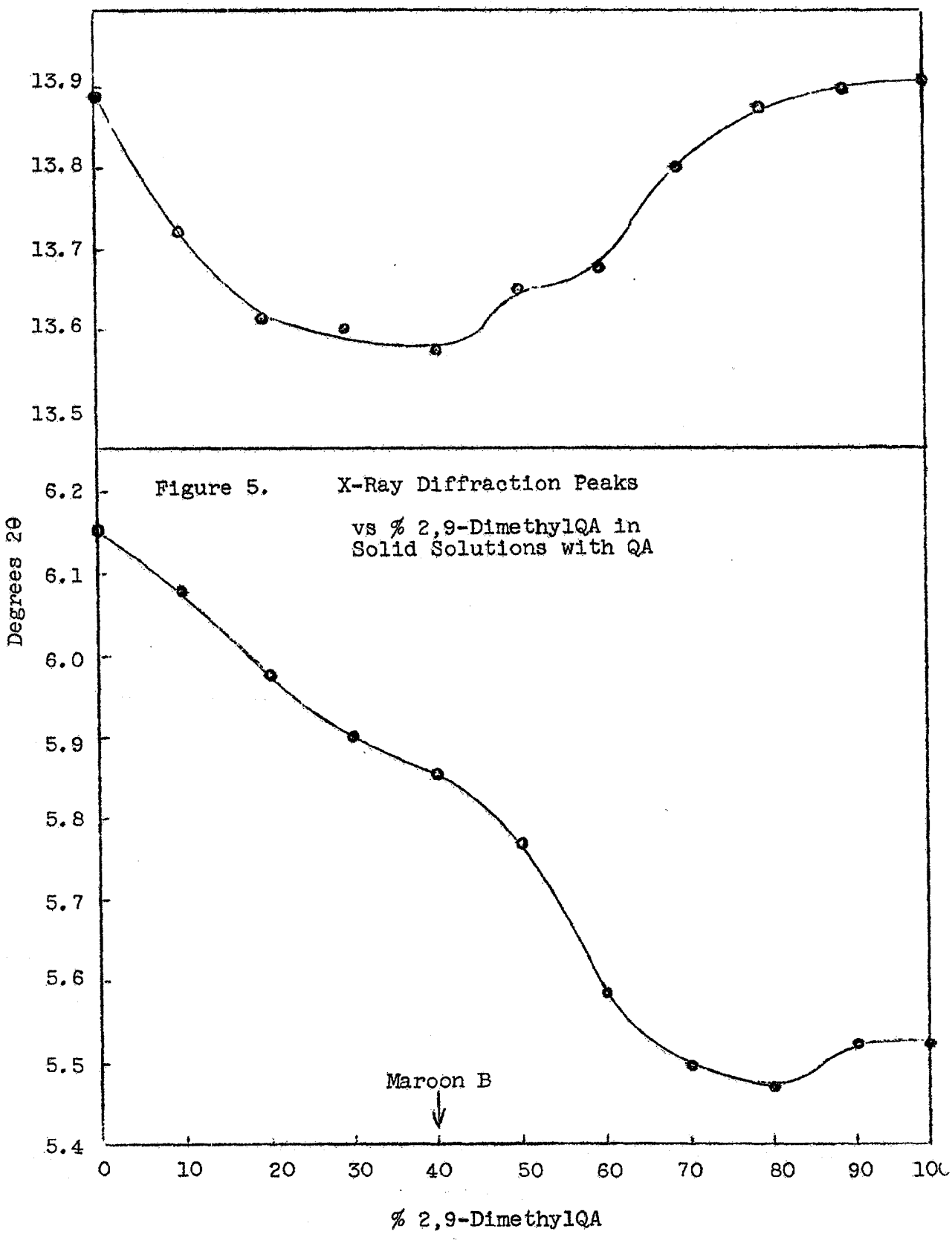


Figure 5. X-Ray Diffraction Peaks vs % 2,9-DimethylQA in Solid Solutions with QA

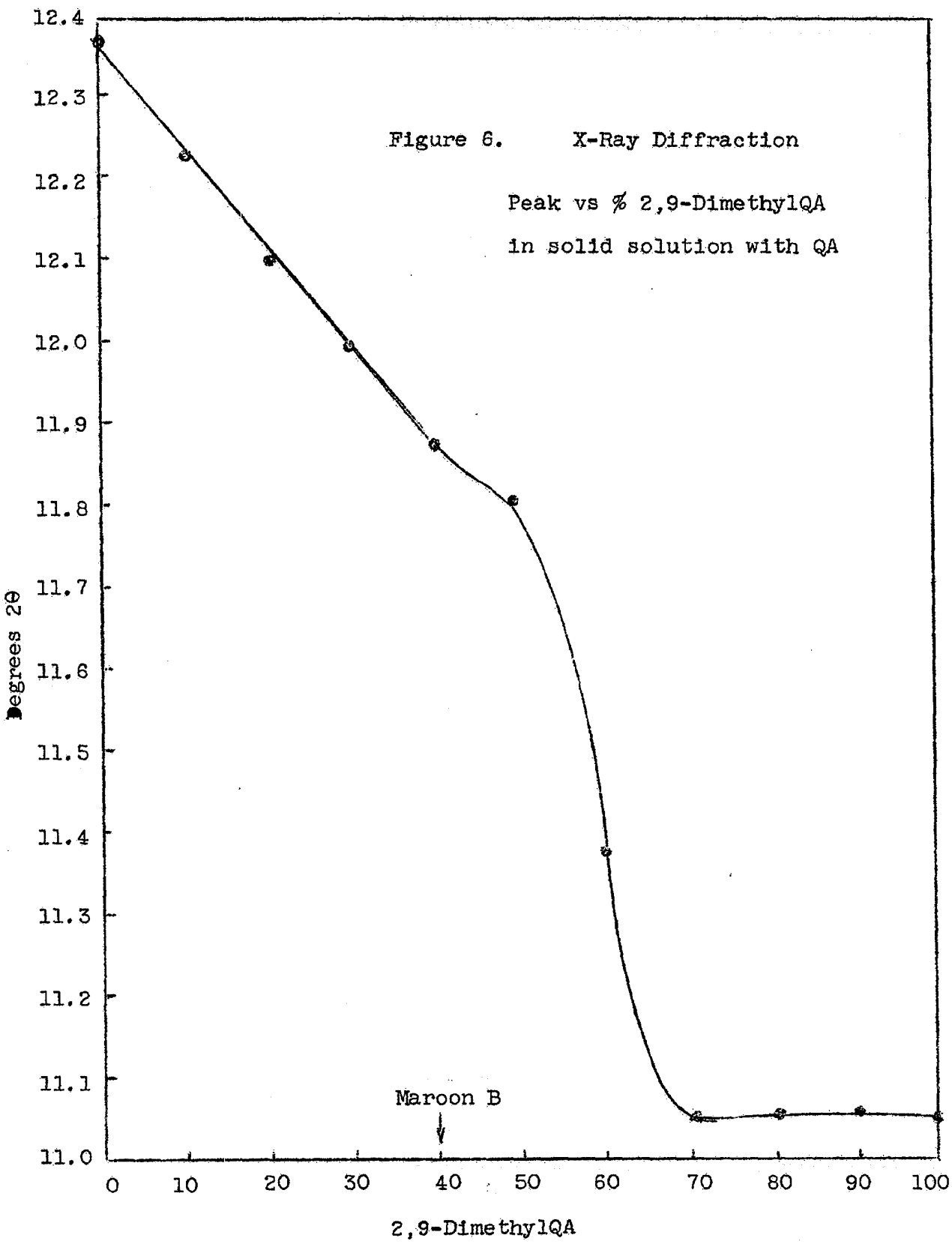


Figure 6. X-Ray Diffraction

Peak vs % 2,9-DimethylQA

in solid solution with QA