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REACTION OF TRICHLOROACETIC ACID WITH P-CRESOL

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P-クレゾールに対するトリクロル酢酸の反応

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The authors found a method to prepare a new type of pigment from p-cresol reacted with trichloracetic acid and studied about the chemical structure of the new pigment.

1 INTRODUCTION

Though p-cresol is treated by the usual method of preparing polymethylaurins, we can not obtain the expected pigment, but only black substances are produced. In this study the authors found that the reaction could be smoothly promoted to generate the pigment if some more amounts of NaOH were added again during the process. The product was examined by elementary analysis, UV,V and IR spectroscopy.

2 PREPARATION OF THE PIGMENT

2g of p-cresol was taken in a test tube, 6ml of 50% trichloroacetic acid, 7ml of 33% NaOH added and heated at 80-85℃ for 5-10 minutes on a waterbath. At this stage the solution became deep red and a lot of yellow crystals separated and were identified as 6-oxy-3-methyl benzaldehydes. 7ml of the same NaOH solution was added and kept being heated at 90℃ for about 30 minutes. Then the total mass became dark red. The red crystals were filtered using a Buchner funnel. But the authors found that they were mostly cmposed of aldehydes. And so the red filtrate was neutralized with dil. HCl to precipitate the pigment. The precipitates were washed well with water until the mineral substances were almost perfectly removed. Then they were dissolved in ethylalchol and developed with a mixed solvent of ethyl alcchol :water (2:1) through an active alumina packed column of 20×2 cm size. The effluent was evaporated, yield :8 %. On the other hand the top layer of the alumina column absorbed a large quantity of

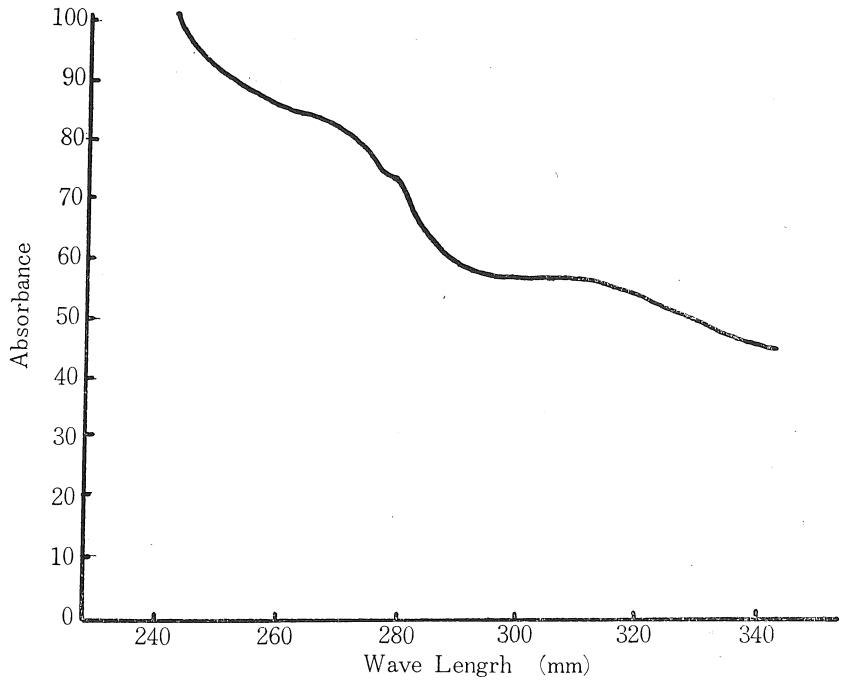

Fig. 1. 1 UV spectrum of the new pigment

pigment. And so this part was cut off and extracted with dil. NaOH at 80℃ for a short time. By this treatment almost all of the adsorbed pigments could be recovered, and were treated by the same method described above, yield :12 %. Thus the total yield became 20 %. Elementary analysis gave the same values in the two caces of preparation.

3 UV, V AND IR SPECTROSCOPY

An alcoholic solution of this pigment gave a characteristic absorption at 470 mm as seen in Fig. 1. 2. But all other polymethyl-aurins had their peaks around 550 mm. Because of this reason we can consider that the configuration of this pigment is quite different from the others. As seen in Fig. 2, methyl, hydroxyl and aldehyde radicals gave their characteristic absorptions at 1870, 3400-3200 2800 cm^{-1}each. The absorption by the aldehyde radical is rather small owing to its interaction with an adjacent OH.

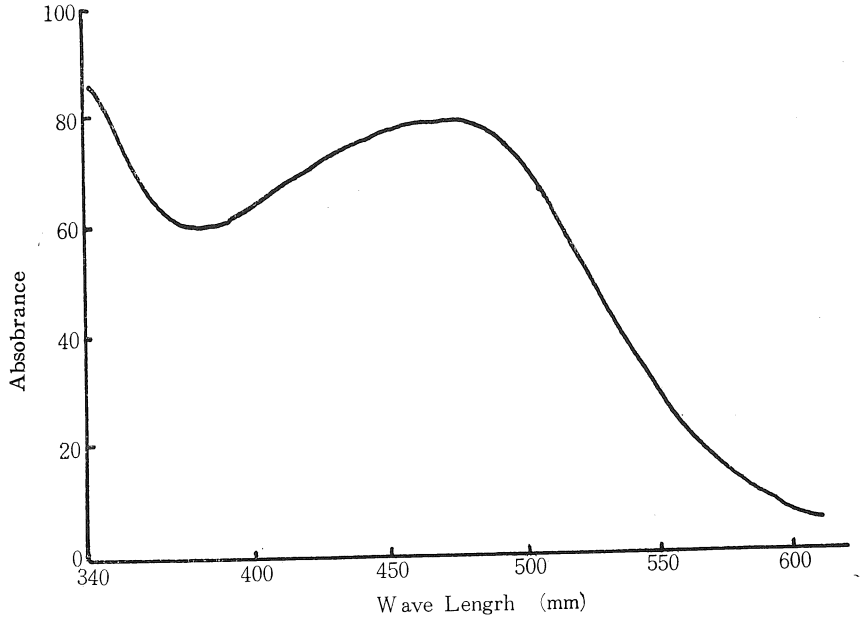

Fig.1 .2 UV and V spectrum of the new pigment

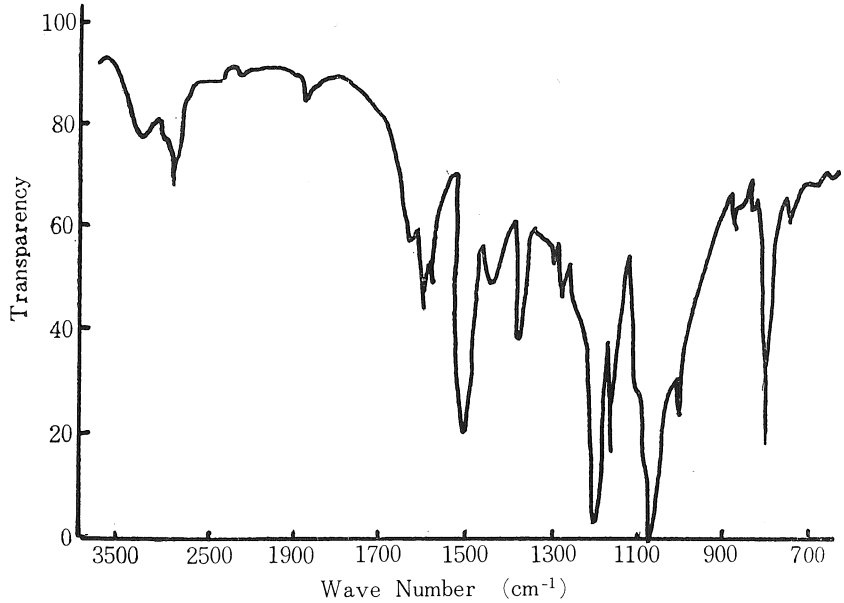

Fig.2 IR spectrum of the new pigment

4 CONSIDERATION ON THE MECHANISM OF REACITON AND THE CHEMICAL STRUCTURE OF PIGMENT

When p-cresol reacts with trichloroacetic acid in an alkaline medium, 9-oxy-3-methylbenzaldehyde is produced at first and then reacts with another trichloroacetic acid to generate a pigment. The mechanism is considered like those in Fig. 3.

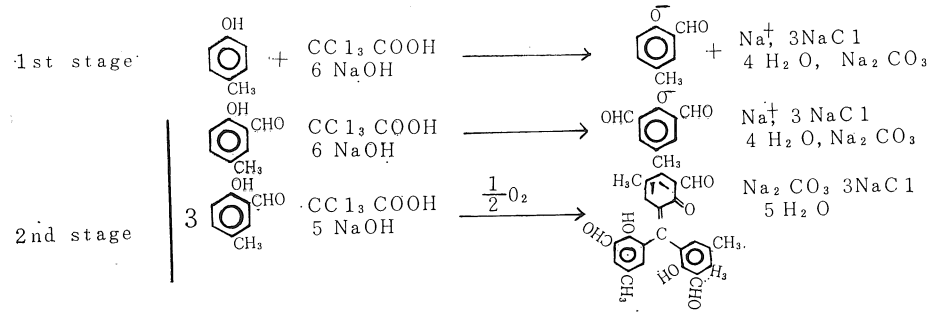

Fig. 3 Mechanism of the Reaction

Besides the two kinds of pigment shown in Fig. 3, we can consider two more which include one or no CHO in a molecule. The results of elementary analysis are shown in Table 1.

Table 1 Elementary Analysis

	C %	H %
$C_{25}H_{20}O_6 \cdot 2H_2O$	66.3	5.3
$C_7H_{10}O_3$	66.5	4.9
Found	65.6	5.6

This data suggest that the chemical structure can be a) or b) in Fig. 4.

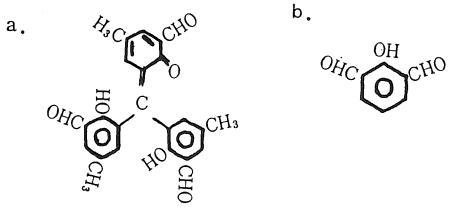

Fig. 4 Chemical Structure assumed

The chemical structure b) has no chromophoric group. And so a) is the most probable one for the pigment. This is a new type pigment different from any kind of polymethylaurins, for the reason that its central carbon is bonded with three phenolic compounds at their ortho positions, not para as seen in Fig. 4 a). And this pigment is denominated as 3-aldehyde-5-methylbenzochinon - (1, 2) - bis- (3-alde hyde- 4-oxytoluyl) -methid - (5) .

Acknowledgment

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References

1) Some parts of this study were presented at the fall general meeting of Japanese chemical society in Tokyo, October 1971.
2) K.Kihara and others: Kogyo Kagaku Zasshi. 73,2,110 (1970)