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On the Purification and Sublimation of Anthracene

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Abstract

The purification of crude anthracene has been carried out by washing with acetone and benzene, distilling with ethylene glycol and zone refining. The degree of purification at each stages have been determined through measuring the fluorescence spectrum of anthracene, from which we have ascertained that the distillation pocess is the most effective one to exclude impurities, as far as the fluorescence spectra do concern.

The purified anthracene has been sublimated in order to obtain flaked single crystals, using different temperature distribution of furnace and under different pressure of nitrogen gas. With this experiment, we have established the most suitable conditions for the crystal growth.

I. Introduction

We have so many experiments not only on optical and electrical properties of anthracene,[1)] but also on interaction with α, β-rays, neutron and other high energy particles for the use of scintillation counters.[2)] As for the laser research, anthracene has been successfully used as double-photon absorption material of ruby laser light[3)] and recently the fine structure of Q-switched laser pulse was recognized using this material.[4)]

Anthracene obtained from commercial source, contains impurities of similar molecular structure such as tetracene, naphthalene and so forth. The purification of anthracene has been carried out through various chemical methods, and further purification has been done through zone refining. The chemical purification process includes such methods as washing in acetone, recrystallization from benzene, chromatographic purification and azeotropic distillation with ethylene glycol. The anthracene adopted for scintillation-use is said to be obtained after the distillation process, but the degree of purification in each treatment is rather ambiguous.

Therefore, we have examined in detail the purities of anthracene obtained by washing with acetone and benzene, azeotropic distillation with ethylene glycol and zone refining. From the measurement of the u.v. light excited fluorescence from

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anthracene we have confirmed that the distillation process is the most effective to eliminate impurity of tetracene which yields most strong influence upon the fluorescence spectra of anthracene.

So far, single-crystallization of anthracene has been carried out successfully by using three methods; Bridgman method,[5] recrystallization from solution[6] and sublimation.[7] In the present experiments, we have examined the sublimation method, especially allowing for special care for temperature distribution of the furnace and the nitrogen gas pressure variation during crystallization. Finally an attempt to obtain larger crystals by sublimation is presented.

II. Experimentals

1) Chemical Purification

Commercially obtained anthracene (Kishida K.K.) is washed with acetone and benzene to eliminate impurities soluble in these solutions. Then the washed anthracene is azeotropically distilled with ethylene glycol in order to remove mainly carbazole impurity. The distillation is done at approximately 220°C, with the mixed solution of anthracene 3: ethylene glycol 7 in weight.

After the distillation is over, partially purified anthracene containing ethylene glycol is obtained. The elimination of ethylene glycol to obtain purified anthracence in powdered state is carried out by drying on the filter paper, washing with water and re-drying at approximately 65°C for hours. This treatment is done with the consideration that ethylene glycol is much more soluble in water than in anthracene.

2) Zone Refining

Powdered anthracene is packed into a glass tube, which is then throughly evacuated. The anthracene is consolidated to form a compact mass of about 70% of the whole tube length. Nitrogen gas is admitted to a pressure of approximately 0.5 atmospheric pressure and then the tube is sealed. The nitrogen gas prevents the bumping of the molten anthracene. The sealed tube of about 20 cm long is pulled up along the furnace at a speed of 0.8 cm/h. The furnace, as shown in Fig. 1, consists of 18 successive zones, and is inclined about 50° to the horizontal line. Each zone, 1 cm long and 5 cm apart, is constructed with nichrome wire and is heated up to 250°C. Using this furnace,

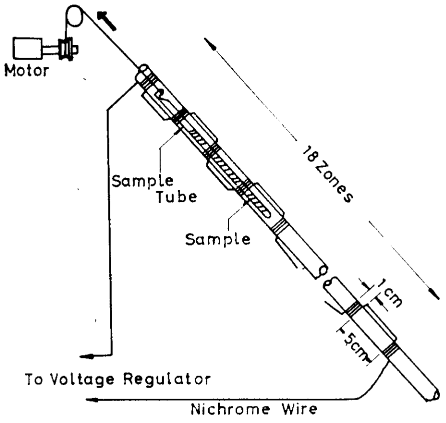

Fig. 1. Zone Refining Apparatus.

operation of 18 zone refining can be made in succession and then the impurities are segregated to the top and the bottom of the sample.

3) Sublimation Process

The purified anthracene of about 0.5 gr. is packed in a glass tube, which is, after being evacuated by a rotary pump, filled up by the nitrogen gas. The gas pressure is varied from 10^{-2} mmHg up to 3 atmospheric pressures. When the gas pressure becomes above 1 atmospheric pressure, the glass tube is closed by mechanical valves instead of sealing. The glass tube is then put in the vertical furnace in which the source part is kept at approximately 240°C. The temperature of the crystal-growing part is rather critical as will be discussed in Sec. III; it extends between 75 and 125°C.

4) Luminescence Measurements

The degrees of purification at different processes in the form of powder, flake and solution are determined by the u.v. excited luminescence spectra of anthracene. Ultra violet light of 365 mμ is carefully selected from Xe lamp through the prism monochromater. Luminescence spectra are obtained using Hitachi R-139 spectrometer with Hamamatsu TV R-106 photomultiplier of S-19 type photocathode.

III. Results and Discussions

1) Sublimation

We have examined in detail the effect of nitrogen gas pressure on the crystal growth. The samples used for sublimation are obtained after chemical purification with ethylene glycol and then performing zone refining.

As the nitrogen gas pressure increases, the rate of sublimation decreases. For instance, in the case of 3 atmospheric pressures, about 6.5 hours are required to sublimate 0.5 gr. anthracene completely, whereas, in 10^{-2} mmHg it takes only 0.5 hour. In contrast to the above phenomena, produced crystal forms become worse when gas pressure becomes low.

When the pressure is less than 0.5 atmospheric pressure, the rate of crystal growth becomes so fast and then the sublimated crystal is inclined to become powdered form or a very small single crystal. When the gas pressure becomes high, the strong nitrogen gas convection is formed between the high and the low temperature region of the furnace. This strong convection destroys the once grown crystals into pieces. From the above results, we may conclude that the most suitable nitrogen gas pressure to sublimate single crystal of considerable size may be between 1 and 0.5 atmospheric pressure.

The temperature of the sublimated region is critical, between 75 and 125°C.

So we can hardly point out the exact position from where the crystal grows. Whereas, sublimation rate determined by the source temperature, is rather insensitive compared with the temperature of the crystal-growing region.

To overcome this defect, the following method has been tried to make larger single crystals. By pulling the sample tube upward slowly along the furnace, the crystal-growing region moves downward and the sublimated crystal grows larger in length. Actually, with this method, we obtained anthracene single crystal of 0.06 mm thick, 10 mm wide and 20 mm long, while in the static method, only 5 to 10 mm in length is formed. With the improvement of the furnace temperature distribution and pulling speed, larger crystals will probably be obtained with the above mentioned method.

2) *Luminescence Spectra*

The anthracene obtained in various stages of purification takes the form of powder or flake, each of which can be solved in ethanol. The forms of anthracene do influence only on the self absorption phenomena of the bulk material, as will be discussed in detail related to Fig. 5. The comparisons of the luminescence spectra of anthracenes in powder, flake and solution are made in Fig. 2 to 5, in which each luminescence curve is normalized at its highest peak. Treatment of each sample is summerized in Table 1.

In Fig. 2, luminescence spectra of powdered anthracene are shown. #1 and #2 have distinct yellow peaks and small subsidinary blue peaks, whereas, #3 and #4 show strongest peaks in the blue luminescence region. Yellow peaks beyond 500 mμ are considered to correspond to tetracene and blue peaks around 450 mμ or shorter wavelength region, to anthracene itself.[8] This leads us to the conclu-

Table 1. Treatment of Each Sample.

Sample Number	Sample Form	Washing	Distillation	Zone Refining	Sublimation
#1	P	/	/	/	/
#2	P	1	/	/	/
#3	P	1	2	60	/
#4	P	1	3	/	/
#5	F	1	/	Several	/
#6	F	1	2	60	1
#7	S/0.01	1	2	60	/
#8	S/0.01	1	2	60	1
#9	S/0.01	1	3	/	/
#10	S/0.02	1	3	60	1

(Note) P—Powder, F—Flake, S/0.01—Solved in ethanol (0.01 weight %), / denotes "process not done," and numbers denote frequency of operation. (Sublimation is done under 1 atmospheric pressure of nitrogen.)

sion that tetracene impurity involved in the commercially obtained anthracene cannot be eliminated with the treatment with acetone and benzene.

Fig. 3 shows luminescence spectra of flaked anthracene. In #5 yellow peaks of tetracene are of approximately 70% in intensity compared with the anthracene highest peak, while, in #6 we can hardly recognize the peaks of tetracene. The results obtained in Figs. 2 and 3 suggest that one distillation rather than several or more zone refining processes will be more effective to remove the tetracene impurity.

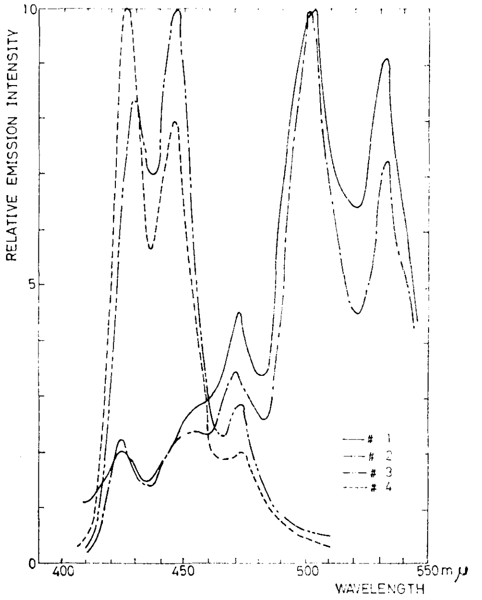

Fig. 2. Luminescence Spectra of Powdered Anthracene at Different Stages of Purification.

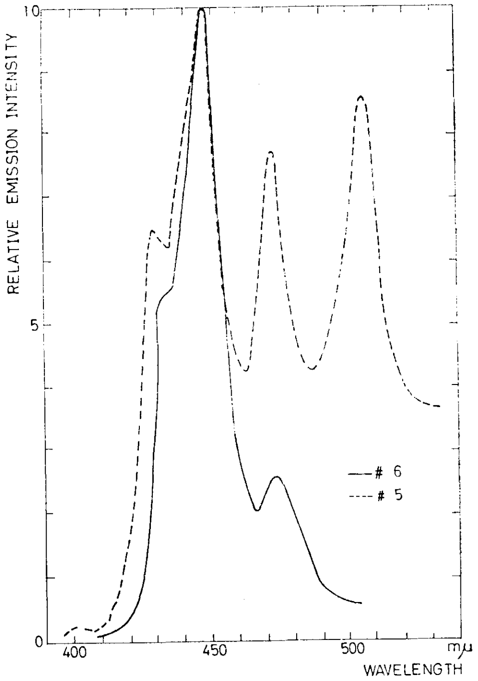

Fig. 3. Luminescence Spectra of Flaked Anthracene at Different Stages of Purification.

The comparison of the results obtained by the three times distillations, and the twice distillations followed by zone refining and sublimation is shown in Fig. 4. We cannot find out remarkable difference between the luminescence spectra of different samples.

Next, we shall compare, as shown in Fig. 5, luminescence spectra of purified anthracenes in different crystal forms. The powdered anthracene spectra are shifted to shorter wavelength region than the flaked one. Furthermore, the less the anthracene concentration, the higher becomes the peaks in the shorter wavelength region. In other words, the peaks of the anthracene luminescence are

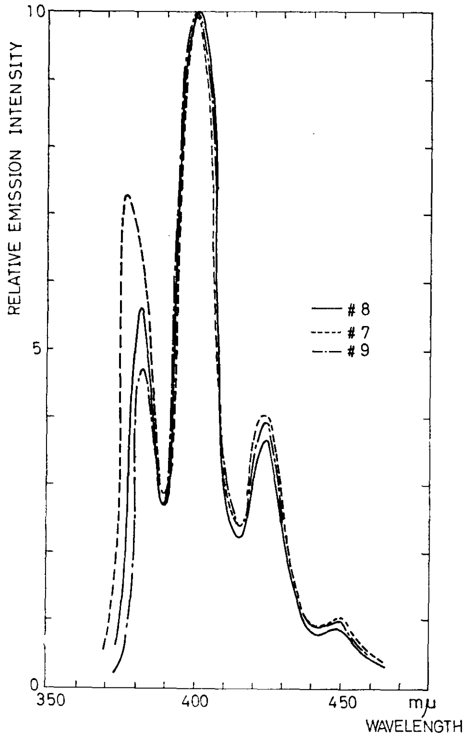

Fig. 4. The Effect of Zone Refining and Sublimation on the Luminescence Spectra of Anthracene Solution in Ethanol.

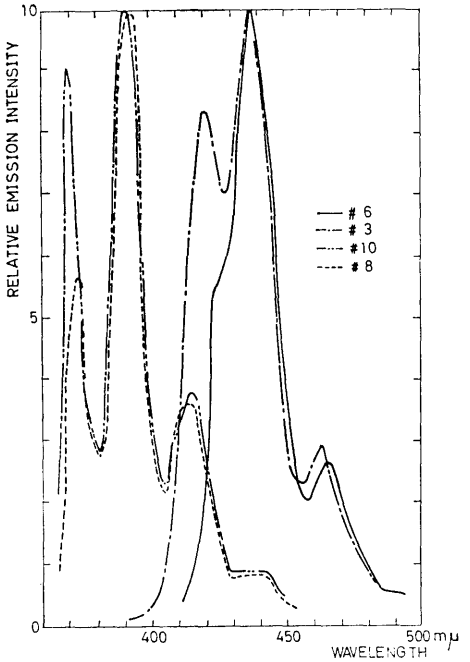

Fig. 5. Luminescence Spectra of Purified Anthracene in Powder, Flake and Solution.

inclined to shift to shorter wavelength region as anthracene molecule decreases in number.

The above mentioned phenomena may be well explained by the self absorption effect,$^{9)}$ as will be shown below. In anthracene molecule, the absorption spectrum shows a "mirror-image" structure around about 400 mμ of luminescence spectra.$^{10)}$ Furthermore, the absorption coefficient increases with the number of anthracene molecules. Therefore, the reabsorption of luminescence in anthracene is stronger in the shorter wavelength region of luminescence and for more dense density of anthracene molecule. Then the peaks in the shorter wavelength region will become predominant in solution rather than in solid.

Finally, it should be noted that Dr. Ohba and his collaborators in our Department of Instrumentation Engineering, have succeeded in confirming the double-photon absorption of ruby laser light by our best purified sample of anthracene.

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