

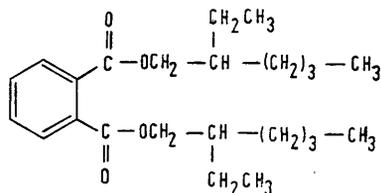
Caution against Contamination of a Phthalate from a Silicone Rubber Tube

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Introduction

Rubber tubes are often used in chemical experiments, which are applied for a circulation of cooling water, transfusing a gas, a solvent and a solution, exhausting a gas generated in a reaction and so on. Recently a silicone rubber tube can be bought instead of a black rubber one, because it is said that it is superior in durability, heat-stability and transparency. In the process of concentration of a solution, a rubber tube is ready for the continuous concentration with a rotary evaporator to connect the solution line from a batch to it.



In this time it was tried to concentrate the extracted n-hexane solution with a rotary evaporator, sending it continuously into the rotary vessel of it through about 30 cm in length of the silicone rubber tube, which was made by Nippon Rikagaku Kikai Co., Japan, connected to the glass inlet tube of the evaporator. And from the residue, a transparent oily material was obtained after isolation and purification, which was later extracted directly from the silicon rubber tube with n-hexane.

So both were identified bis (2-ethylhexyl) phthalate (I), which was used for a plastic agent when the silicone rubber tube was made.

All chemist in experiments then must take caution against contamination of the phthalate when a silicone rubber tube is applied for transfusing organic solvents and solutions.

Experimental and Results

Gas chromatograms were taken by a Shimazu GC-6A, FID, connected with a 2.0 m x 0.5 cm stainless steel column packed with SE-30 at 275°C, the carrier gas was helium at 4 Kg/cm² (approx. 14 ml/min). The ultra violet absorption spectrum was measured by a Hitachi 100-60 connected with a recorder. Infrared spectra were taken by a JEOL IRA-1 spectrometer. Nuclear magnetic resonance spectra for ¹H were recorded using a Hitachi R-40 90 MHz spectrometer using tetramethylsilane as an internal reference. The melting points were measured with a Meihoh automatic thermal analyser MR-2.

The elementary analysis, nuclear magnetic spectra for ¹³C by a JEOL JNM-FX 100 and the mass spectrum by a Hitachi RMU-7 were measured by staffs of the Institute of Physical and Chemical Research, Hirosawa, Japan.

All solvents used for extraction and recrystallization were distilled once before use and of reagent grade quality commercially in Japan.

1. Extraction and Purification

Constituents of 5 Kg of a certain plant small fruits was extracted with 6 l of n-hexane, and the extracted solution was filtered with a filter paper and the filtrate was concentrated continuously with a rotary evaporator

as described above. The residue was separated to 10 fractions by a silica gel (Kiesel Gel 60 Merck) column (3.7 × 40.0 cm) chromatography eluted with solvents of n-hexane: benzene (4:1 and 1:1 v/v), benzene, benzene: ethyl acetate (1:1 v/v), ethyl acetate and n-butanol, successively. From the eluate of benzene, 3.7 g of residue was obtained and it was again chromatographed with a silica gel (Kiesel Gel 60 Merck) column (2.2 × 11.0 cm) which was eluted with ethyl acetate and then acetone consequently, the four fractions (1, 2, 3 and 4) were obtained. The residue of the fraction 2, which was transparent oily, was shown one spot on Tlc (Wakogel B-5), the R_f values were 0.68 and 0.67, developed with chloroform:acetone (7:3 v/v) and benzene:acetone (4:1 v/v), respectively, and one peak on the gas-chromatogram, the retention time was 5.8 min.

On the other hand, about 20 cm in length of the silicone rubber tube (the outside diameter 12 mm, the inside diameter 6 mm) made by Nippon Rikagaku Kikai Co. was cut to pieces of 1 cm in length and they were soaked in 50 ml of n-hexane overnight. The extracted

solution was filtered and the filtrate was concentrated with a rotary evaporator, 5.5 g of transparent oily residue was obtained. And the spectra of the infrared and ^1H nuclear magnetic resonance of this material were compared with them of the fractionated as described above, so it was concluded lately that they were the same material.

2. Elementary Analysis

$\text{C}_{6.23}\text{H}_{10.10}\text{O}$ was composed from the values of the elementary analysis which was shown that C was contained 74.12% and H was 10.08%, their values were taken an average in twice measurements. The molecular formula was made by four times of it, it was therefore $\text{C}_{24.92}\text{H}_{40.40}\text{O}_4$. Then it was considered that the correct molecular formula would be existed in $\text{C}_{24-25}\text{H}_{38-42}\text{O}_4$.

3. Ultra Violet Spectrometric Analysis

In the ultra violet absorption spectrum, three absorption bands were displayed: 203.5 ($E_1^{1\text{ cm}} = 533.2$), 223.0 (221.7) and 273 (32.5) nm, if these bands were due to benzene chromophore, they were characterized

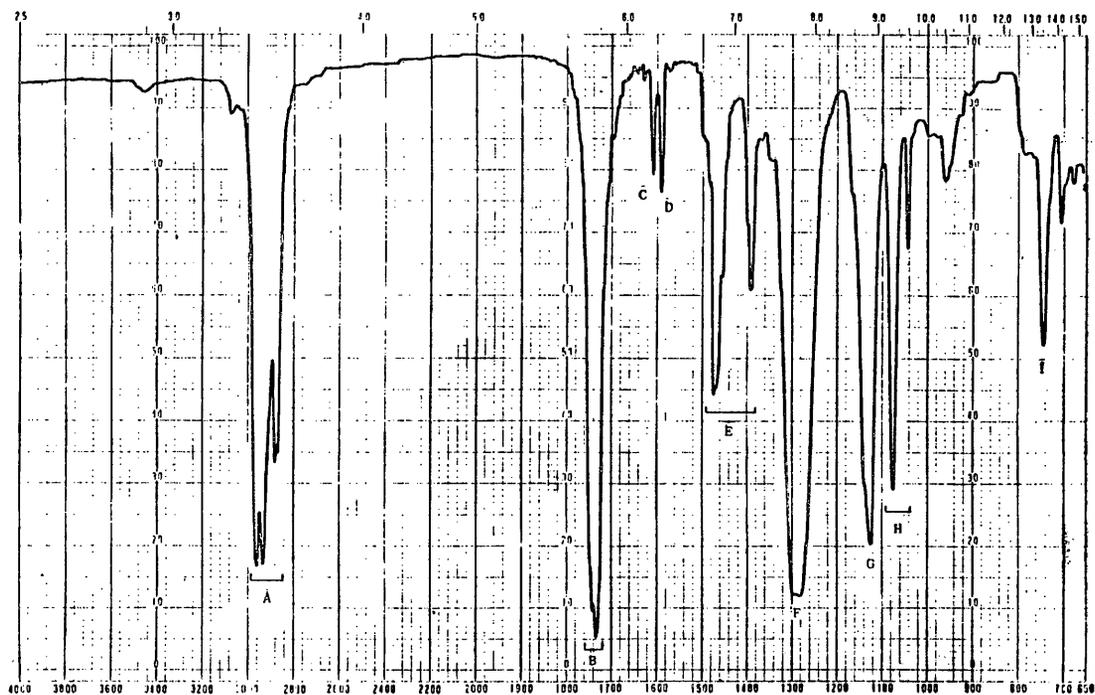


Fig. 1. IR spectrum of the transparent oily material (neat liquid)

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E_2 , K and B-band respectively and originated from $\pi \rightarrow \pi^*$ transitions. And the bands appeared in 223 and 273 nm regions would represent a phthalic acid derivative.

4. Infrared Spectrometric Analysis

It was assigned the peaks from A to I in Fig. 1 to that A. Methyl C-H stretch; 2960, 2940, 2880 and 2870 cm^{-1} , B. C=O stretch; 1735 cm^{-1} , C. Ring C=C stretch; 1610 cm^{-1} , D. Ring C=C stretch conjugated with carbonyl group; 1595 cm^{-1} , E. C-H bent; 1470 cm^{-1} $\delta_s\text{CH}_2$, 1455 cm^{-1} $\delta_{as}\text{CH}_3$, 1390 cm^{-1} $\delta_s\text{CH}_3$, F. Ester CC(=O)-O stretch; 1285 cm^{-1} , G. O-C=C asym. stretch; 1125 cm^{-1} , H. 1:2-substitution; 1075 and 1040 cm^{-1} , and I. Out-of-plane aromatic C-H bent;

745 cm^{-1} , which was four adjacent free hydrogen atoms.

5. ¹H-Nuclear Magnetic Resonance Spectrometric Analysis

In Fig. 2, the peaks at 0.92 ppm was due to methyl groups which were shown a triplet and the integration curve showed 12 H atoms, the peaks in 1.20-1.88 ppm were due to methylene groups and the integration curve showed 20 H atoms, the doublet peak (J=0.05) at 4.23 ppm was due to the methylene group attached to the oxygen atom and the integration curve showed 4 H atoms, and the peaks in 7.40-7.80 ppm were due to aromatic protons which were shown a multiplet and the integration curve showed 4 H atoms.

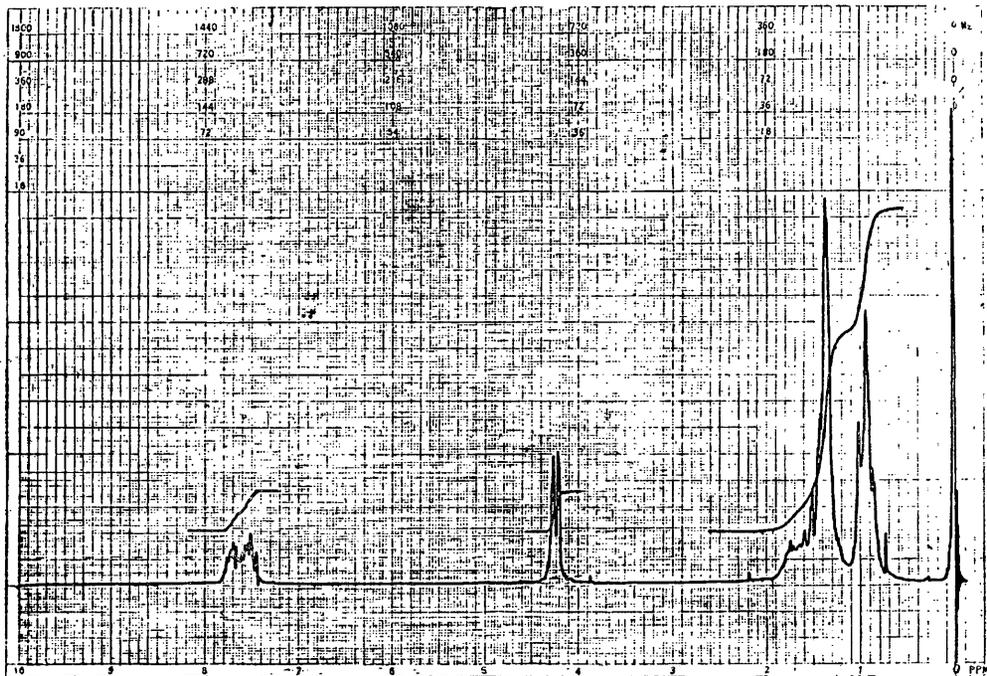
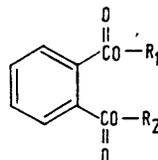


Fig. 2. ¹H-NMR spectrum of the transparent oily material in CDCl_3

From the data of 3-5 analyses, it was considered that the partial structure (II) of the transparent oily material was as follows:



(II)

6. ^{13}C -Nuclear Magnetic Resonance Spectrometric Analysis

From the ^{13}C -NMR spectrum of the transparent oily material with the protons completely coupled and the protons completely decoupled by broad-band noise, the very small peak at 167.76 ppm was assigned to the two equivalent $\text{C}=\text{O}$ groups, the very small peak at 132.52 ppm to the equivalent substituted aromatic carbons, the

large peaks at 130.68 and 128.81 ppm to the remained aromatic carbons, the large peaks at 68.14 ppm to the two equivalent CH_2 groups attached to oxygen atoms, the large peak at 38.75 ppm to the equivalent CH groups, the large and medium peaks at 30.42, 28.95, 23.78 and 23.00 ppm to the CH_2 groups, and the medium peaks at 14.89 and 11.01 ppm to the two kind of CH_3 groups which were two equivalent respectively.

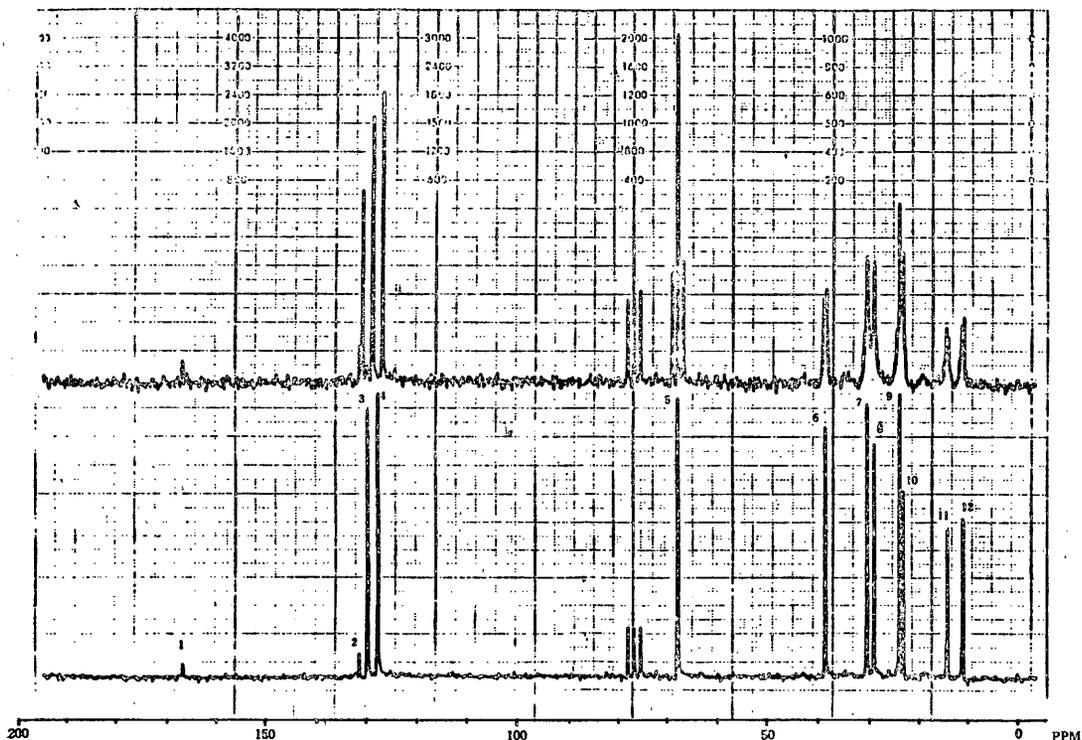
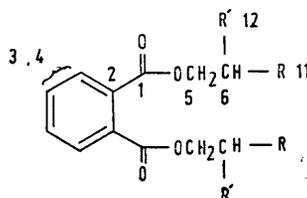


Fig. 3. ^{13}C -NMR spectrum of the transparent oily material with protons completely coupled (above) and protons completely decoupled by broad-band noise (below) in CDCl_3 .

From the data of 5-6 analyses, it was considered that the partial structure (III) of the transparent oily material was as followed:



(III)

7. Mass Spectrometric Analysis

The spectrum of the transparent oily material was given in Fig. 4. In this fragmentation pattern, m/e 149

was characteristic of the fragment of phthalates, and m/e 279 and 261 represented that R₁ and R₂ were both C₈H₁₇.

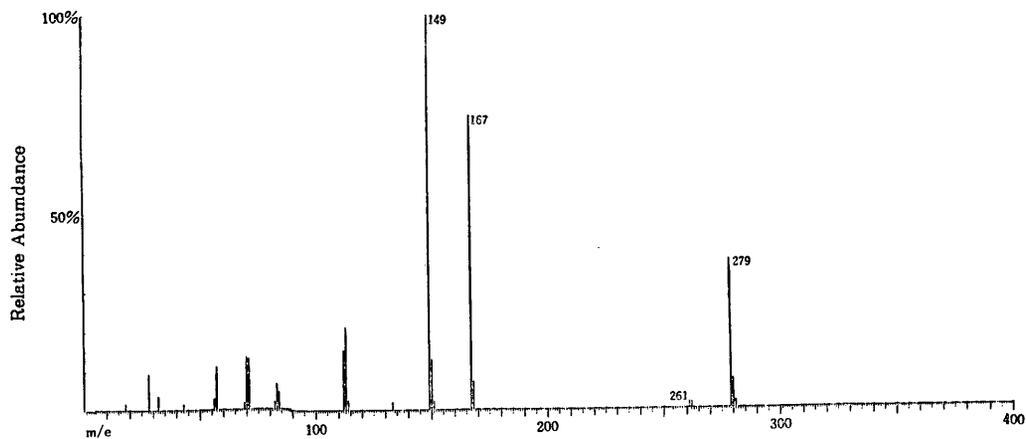
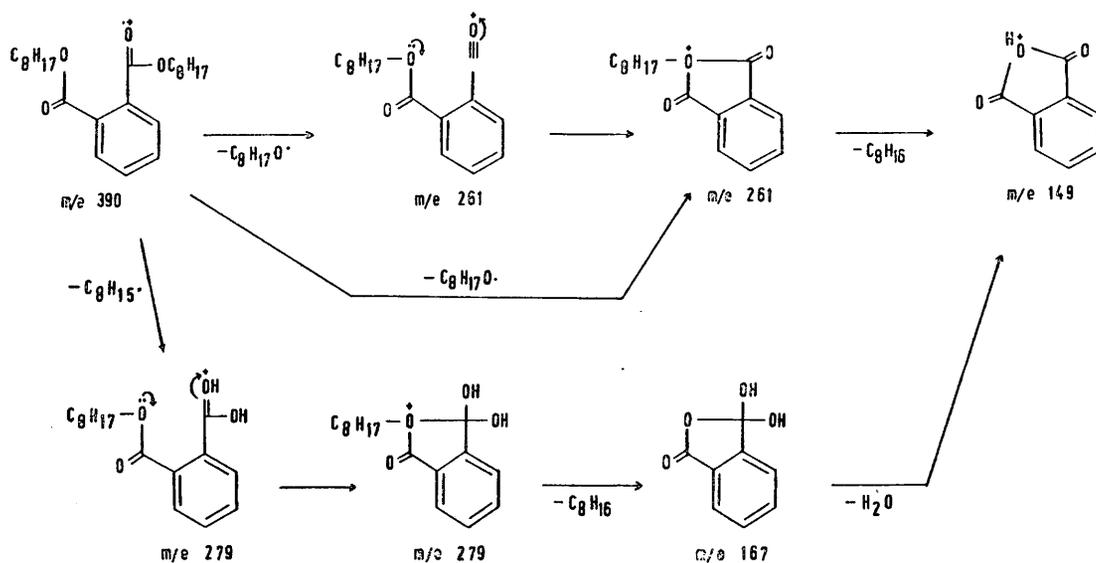


Fig. 4. Mass spectrum of the transparent oily material

Then the molecular formula was proved C₂₄H₃₈O₄, but the molecular peak was not found unfortunately at m/e 390 in the spectrum.



Scheme 1. The mass fragmentation pattern of the transparent oily material

8. Hydrolysis

Two grams of the transparent oily material was dissolved in 50 ml of ethanol containing 2.5 g of potassium hydroxide and refluxed for 5 hr with stirring magnetically. After the reaction mixture was checked

on Tlc, it was concentrated with a rotary evaporator. Fifty ml of water was added and extracted with diethyl ether, the diethyl ether layer was separated, dried over anhydrous sodium sulfate and concentrated with a rotary evaporator, then the oily material was obtained.

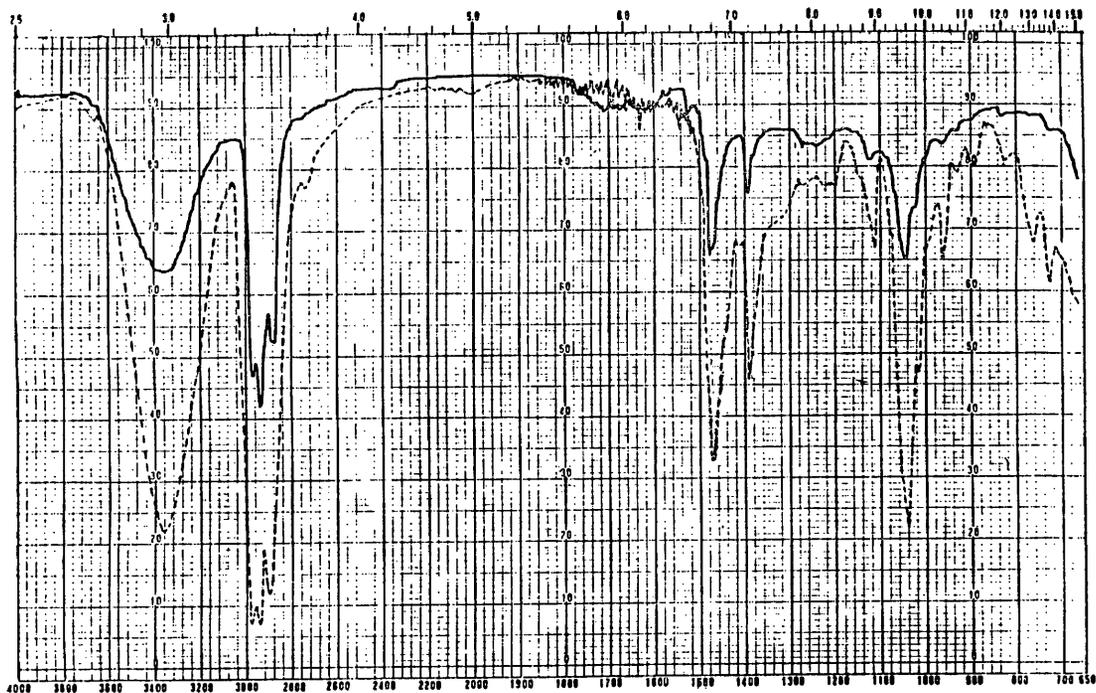


Fig. 5. IR spectrum of the oily material obtained by hydrolysis of the transparent oily material (neat liquid) (solid line), the standard spectrum of 2-ethylhexyl alcohol (neat liquid) (broken line).

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From the infrared spectrum (Fig. 5), it was assigned 2-ethylhexyl alcohol, compared with that of the standard.¹⁾

About the water layer, it was concentrated with a rotary evaporator and acidified with 6 N-hydrochloric acid, then white crystals were obtained, they were

filtered off and measured the melting point and the infrared spectrum which represented phthalic acid (mp. 200.5°C), they were compared with those of the standard²⁾ (mp. 191°C in the sealed tube³⁾ or 210°-211°C⁴⁾) (Fig. 6)

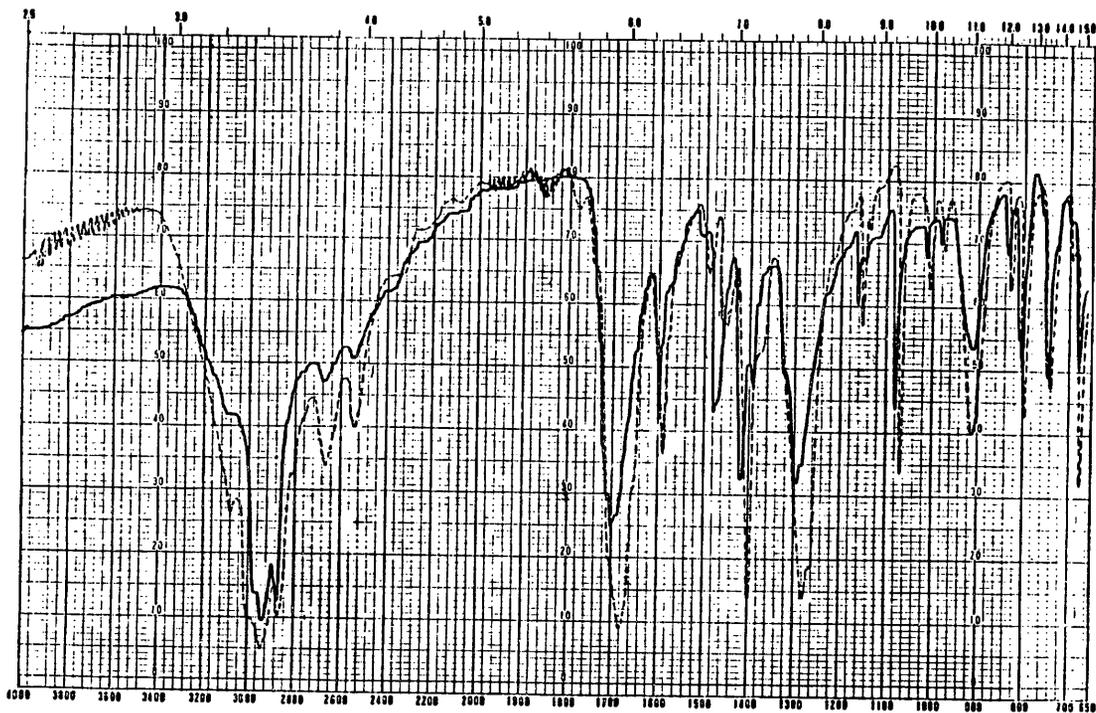


Fig. 6. IR spectrum of white crystals obtained by hydrolysis of the transparent oily material (nujol mull) (solid line), the standard spectrum of phthalic acid (nujol mull) (broken line)

Discussion

Through the series of the experiments and analyses, we have confirmed that the chemical structure of the transparent oily material was bis (2-ethylhexyl) phthalate, and it was extracted from the silicon rubber tube in which it was used as a plastic agent. Then we are apt to obtain it as a contaminant when it is applied for transfusing solvents and solutions from one to another, please take caution against contamination of it in extracts or a residue.

Finally we express our appreciation to staffs of the Institute of Physical and Chemical Research for measurements of the elementary analysis, mass spectra and

¹³C-NMR spectra, to Misses Sayuri Chiba, Michiko Natsume and Chikako Nitta who were students in our laboratory for extractions and separations of the transparent oily material.

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シリコンゴムチューブからのフタル酸エステルの混入に注意

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(昭和58年9月12日受理)

シリコンゴムチューブは近頃よく化学実験に用いられるが、これを有機溶媒や溶液の輸送に使うと、シリコンゴム中に可塑剤として用いられたフタル酸エステルが溶け出し、溶媒や溶液中に混入することになり、貴重な試料中に残るので、その精製に手間どることになる。今回、そのフタル酸エステルがビス(2-エチルヘキシル)フタル酸エステルであることが解明され、シリコンゴムチューブの化学実験での使用の際にその溶出に注意すべきことも明らかとなった。
