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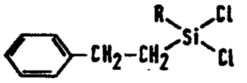
(54) Dichlorosilane derivatives, their production, and their polymerization to polysiloxanes.

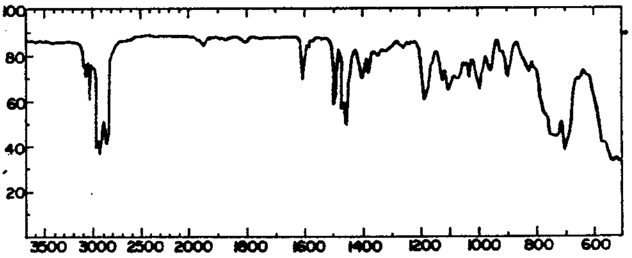
(57) Novel substituted phenethyldichlorosilanes have the general formula



(1)

wherein R is an alkyl group having 3 to 20 carbon atoms or a phenethyl group. Such compounds are produced by reacting a monosubstituted dichlorosilane $RHSiCl_2$ at a temperature of 30 to 200°C with styrene using a catalytic complex of platinum and a phosphine compound. Hydrolysis and polymerization of the substituted phenethyldichlorosilanes (I) yields polysiloxanes with good heat-resistance and other desirable characteristics.

FIG. I



Croydon Printing Company Ltd.

"DICHLOROSILANE DERIVATIVES, THEIR PRODUCTION, AND THEIR POLYMERIZATION TO POLYSILOXANES"

The present invention relates to dichlorosilane derivatives, their production, and their polymerization to polysiloxanes. More particularly, the dichlorisilane derivatives with which we are concerned are substituted phenethyldichlorosilanes.

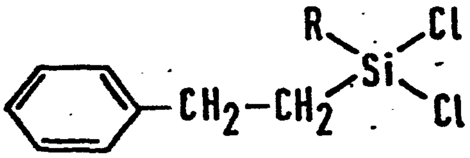
Diorganodichlorosilanes are very important compounds in the silicone resin industry but only relatively few compounds such as dimethyldichlorosilane and diphenyldichlorosilane are actually used on an industrial scale. Methods for producing diorganodichlorosilanes include one which utilizes Rochow's process and one which utilizes a Grignard reaction, but any of the known methods produces a large amount of by-products and it is thus difficult to obtain diorganodichlorosilanes in good yield using the methods currently available.

With the recent developments in the silicone resin industry, it has become appreciated that other diorganodichlorosilanes are desirable. For example, diorganodichlorosilane compounds of the type $R^aR^bSiCl_2$ which contain an alkyl substituent R^a and an aralkyl substituent R^b would be useful as bifunctional monomers for polysiloxanes. However, the only such $R^aR^bSiCl_2$ compound which has been commercially produced up until now is CH_3SiCl_2Ph, Ph being a phenyl group. Moreover, a search through the chemical literature reveals that this example of the $R^aR^bSiCl_2$ compounds is supplemented only by those in which R^a is a methyl or ethyl group and which are of the formulae $C_2H_5SiCl_2(CH_2CH_2Ph)$, $C_2H_5SiCl_2(CHCH_3Ph)$, $C_2H_5SiCl_2[(CH_2)_3Ph]$, $C_2H_5SiCl_2$-$[CH_2CH(CH_3)Ph]$, $C_2H_5SiCl_2[(CH_2)_4Ph]$, and $C_2H_5SiCl_2$-$[CH(CH_3)CH_2CH_2Ph]$; see Chemical Abstracts 54, 22435 and 53, 17028.

It is the present state of the art that there are no known asymmetrically-substituted compounds $R^aR^bSiCl_2$ in which R^a and R^b both have more than 2 carbon atoms. In addition, there are no methods available for producing any such compounds.

We have been continuing our research work in various ways in order to overcome the above mentioned problems in this field of art, and have succeeded in the preparation of compounds which have previously not been known. The compounds which we have prepared are suitable as bifunctional monomers for production of polysiloxanes.

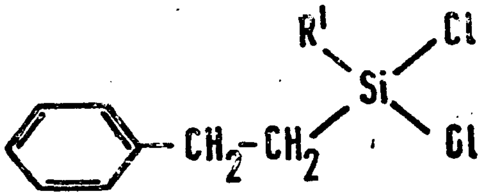
The compounds of the present invention are substituted phenethyldichlorosilanes represented by the general formula



(1)

wherein R is an alkyl group having 3 - 20 carbon atoms or a phenethyl group. The present compounds thus share in common the fact that they are diorganodichlorosilanes substituted by different organo groups which both possess 3 carbon atoms or more.

More particularly, the present compounds include alkylphenethyldichlorosilanes represented by the general formula

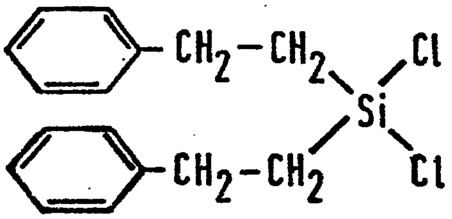


(II)

wherein R' is an alkyl group having 3 - 20 carbon atoms.

Concrete examples of compounds of the formula (II) are propylphenethyldichlorosilane, isopropylphenethyldichlorosilane, butylphenethyldichlorosilane, isobutylphenethyldichlorosilane, pentylphenethyldichlorosilane, isoamylphenethyldichlorosilane, hexylphenethyldichlorosilane, heptylphenethyldichlorosilane, octylphenethyldichlorosilane, nonylphenethyldichlorosilane, decylphenethyldichlorosilane, undecylphenethyldichlorosilane, dodecylphenethyldichlorosilane, tridecylphenethyldichlorosilane, tetradecylphenethyldichlorosilane, hexadecylphenethyldichlorosilane, octadecylphenethyldichlorosilane and eicosylphenethyldichlorosilane.

The compounds of the present invention also include diphenethyldichlorosilane represented by the formula



(III)

The method we provide for producing the compounds of the present invention comprises reacting at a temperature of 30 to 200°C a monosubstituted dichlorosilane having the general formula R^3HSiCl_2, where R^3 is as defined above, with styrene in the presence of a complex of platinum and a phosphine.

Where R^3 in the monosubstituted dichlorosilane is an alkyl group having 3 to 20 carbon atoms it is preferred that the reaction with styrene is effected at 30 to 110°C. The reaction time is not critical but is usually 1 to 60 hours. The required starting material, a monoalkyldichlorosilane of formula R'-$HSiCl_2$, R' being as defined above, is preferably prepared by the addition reaction with dichlorosilane itself of an α-olefin having 3 to 20 carbon atoms. For example such a starting material can be obtained by reacting dichlorosilane and an α-olefin having 3 to 20 carbon atoms in the presence of a complex of a phosphine compound and a transition metal of group 8 at a temperature of 30 to 200°C. Conviently the reaction is carried out for 1 to 60 hours at atmospheric or greater pressure. Where the transition metal is other than platinum the reaction is preferably effected at 50 to 200°C and the catalyst then separated off before the subsequent reaction with styrene. On the other hand, where the transition metal is platinum then the preferred reaction temperature is 30 to 110°C. Furthermore, the complex need not be separated off but can be retained in the liquied as the catalyst for the subsequent reaction with styrene.

Where R^3 in the monosubstituted dichlorosilane is phenethyl, the required starting material, monophenethyldichlorosilane, can be obtained by reacting dichlorosilane with an equimolar or excess amount of styrene in the presence of a complex of a transition metal of group 8 and a phosphine. Examples of such complexes include chlorotris(triphenylphosphine)rhodium(I), $[RhCl(PPh_3)_3]$ and tetrakis(triphenylphosphine)platinum(0), $[Pt(PPh_3)_4]$. Suitably the reaction is effected at 30 to 200°C, and when the complex is a platinum complex then it is usually found that monophenethyldichlorosilane alone is obtained if the molar ratio of styrene to dichlorosilane is 1 or less, and that diphenyldichlorosilane is also produced if styrene is present in molar excess. Such reactions may be represented by the following equations (1) and (2):

$$H_2SiCl_2 + 2PhCH = CH_2 \rightarrow (PhCH_2CH_2)_2SiCl_2 \;......(1)$$

$$PhCH_2CH_2SiHCl_2 + PhCH = CH_2 \rightarrow (PhCH_2CH_2)_2SiCl_2 \;....(2)$$

In other words, diphenyldichlorosilane can be produced by reacting dichlorosilane with 2 or more molar equivalents of styrene or by reacting monophenethyldichlorosilane with 1 or more equivalents of styrene, the reaction being effected in the presence of a complex of platinum and a phosphine compound at 30 to 200°C. The preferred reaction time is 0.5 to 60 hours.

The complex of platinum and a phosphine compound employed in the methods of the present invention acts as a catalyst and is preferably tetrakis(triphenylphosphine)platinum(0). The preferred concentration of complex is 1 to 10^{-15}, preferably 1 to 10^{-8}, mol percent per silicon atom.

The production of the substituted phenethyldichlorosilanes can be carried out as a batch, flow-method or half-batch procedure. For example, diphenethyldichlorosilane can be produced by a method in which liquefied dichlorosilane, styrene and the catalytic complex are charged into a sealed reactor, reacted by heating under pressure, and distilling off the product after reaction. Other methods include those in which dichlorosilane is flowed into a reaction vessel containing styrene and a catalytic liquid, or in which styrene and dichlorosilane are counter-flowed through a fixed bed supporting a catalyst on a carrier.

A characteristic feature of the methods described is the use of dichlorosilane and/or a mono-substituted dichlorosilane as starting material for production of the substituted phenethyldichlorosilanes. In such methods it is to be noted that the hydrogen directly joined to the silicon of dichlorosilane or of the mono-substituted dichlorosilane adds only to the α-position of styrene to form the product. It is of great advantage that the isomer in which the above mentioned hydrogen adds to the β-position of styrene is not formed. Moreover we have found that other by-products are not obtained and that the desired substituted phenethyldichlorosilanes are typically formed in an extremely high yield.

The compounds (I) of the present invention are novel compounds which can be polymerized using conventional methods to produce polysiloxanes. As is well known, the polymerization involves hydrolysis to give initially the corresponding hydroxy compounds which then readily undergo inter- and intra-molecular condensation. The polysiloxanes obtained using the substituted phenethyldichlorosilanes of the present invention have improved heat-resistance and other desirable characteristic. The compounds of the present invention can thus be used for improving the heat-resisting and other properties of silicone oils, rubbers and varnishes which are used as electrical insulating materials, lubricating oils, water-repelling agents, paints, release agents etc.

The present invention will now be illustrated by the following non-limiting specific Examples; comparative examples are also given. In the examples reference is made to the accompanying drawings, in which:

Figures 1 and 2 are respectively the infrared (ir) and nuclear magnetic resonance (nmr) spectra of n-hexylphenethyldichlorosilane produced in Example 1;

Figures 3 and 4 are respectively the ir and nmr spectra of n-dodecylphenethyldichlorosilane produced in Example 2; and

Figures 5 and 6 are respectively the ir and nmr spectra of diphenethyldichlorosilane produced in Example 4.

Example 1

3.80 g (20.5 millimol) of n-hexyldichlorosilane, 2.00 g (19.2 millimol) of styrene, and 0.023 g (1.92 x 10^{-5} mol) of tetrakis(triphenylphosphine)platinum(0) were introduced into a flask and reacted with stirring by heating in an oil bath at 60°C for 8 hours. Distillation under reduced pressure of the reacted mixture produced 5.6 g (17.5 millimol) of a product shown to be n-hexylphenethyldichlorosilane, $(n\text{-}C_6H_{13})(C_6H_5CH_2CH_2)SiCl_2$.

The n-hexylphenethyldichlorosilane had a boiling point of 120 to 123°C/1mmHg and an n_D^{20} of 1.5009. The elemental analysis was as follows:-

found: C: 57.87%, H: 7.57%, Cl: 23.5%;
theoretical: C: 58.12%, H: 7.66%, Cl: 24.51%.
The ir spectrum of this product was as shown in Figure 1 and the nmr spectrum was as shown in Figure 2.

Comparative Example 1

Reaction was carried out as in Example 1 except that an isopropanol solution of $H_2PtCl_6.6H_2O$ was substituted for th tetrakis(triphenylphosphine)platinum(0). A resinous product formed and no n-hexylphenethyldichlorosilane could be obtained.

Example 2

Reaction was carried out as in Example 1 except that n-dodecyldichlorosilane was substituted for the n-hexyldichlorosilane, whereby a product shown to be n-dodecylphenethyldichlorosilane $(n\text{-}C_{12}H_{25})(C_6H_5CH_2CH_2)SiCl_2$, was obtained.

The boiling point of the product was 165.2 to 168.0°C/2mmHg. The ir spectrum of this product was as shown in Figure 3 and the nmr spectrum was as shown in Figure 4.

Example 3

0.89 mol of 1-hexene, 0.08 mol % (relative to dichlorosilane introduced later) of catalyst, tetrakis(triphenylphosphine)platinum(0), were introduced into a 500 ml pressure-proof stainless steel reactor which was sealed and then cooled with a dry-ice-methanol bath. After introduction into the reactor of 0.64 mol of dichlorosilane through an inlet pipe, the reactor was sealed and reaction was carried out by heating in an oil bath at 100°C for 2 hours with stirring. The reacted liquid was transferred to a flask, 0.64 mol of styrene was added and further reaction was carried out with stirring at 80°C for 4 hours. After the reaction, distillation was carried out under reduced pressure to obtain 0.58 mol of n-hexylphenethyldichlorosilane having a boiling point of 120 to 123°C/1mmHg.

Example 4

25.6 g (254 millimol) of dichlorosilane, 52.3 g (502 millimol) of styrene and 0.295 g (0.237 millimol) of tetrakis(triphenylphosphine)platinum(0) were charged into a 200 ml pressure-proof stainless steel reaction tube as in the procedure Example 3, then heated in an oil bath at 150°C for 16 hours with stirring. Distillation of the reacted liquid under reduced pressure gave 36.0 g of a product shown to be diphenethyldichlorosilane, $(C_6H_5CH_2CH_2)_2SiCl_2$.

The diphenethyldichlorosilane had a boiling point of 140 to 151°C/1.0mmHg. The ir spectrum was as shown in Figure 5. Absorptions are observed for aromatic C-H stretch at 3000 to 3100 cm^{-1} and for deformation of a C-H directly connected to Si at 1260 cm^{-1}, but no characteristic absorption is seen for Si-H in the neighbourhood of 2100^{-1}. The nmr spectrum was as shown in Figure 6. Referreing to the δ scale (ppm), there is no signal corresponding to Si-$\underline{H}$ at 3.0 to 5.0, but signals are seen at 0.99 (corresponding to Si-$C\underline{H}_2$-) at 2.72 ($-CH_2-C\underline{H}_2-C_6H_5$) and at 7.12 ($C_6\underline{H}_5-$). The integration for these signals was in the ratio 4:4:10. In the mass spectra, a parent ion M^+ 308 was observed.

A polysiloxane was then prepared in a conventional manner using the diphenethyldichlorosilane as obtained in this Example. Initial hydrolysis at 60°C give a product of average molecular weight 860 which was shown by ir to include cyclic components formed by intramolecular condensation. This initial product had a refractive index (25°C, D) of 1.570 and a kinetic velocity (25°C) of 280 centistokes. Further reaction at 80°C of 94g of the product with 3g of hexamethyldisiloxane in the presence of 1 ml of 10% aqueous tetramethylammonium hydroxide gave a polysiloxane of average molecular weight 3800.

The polysiloxane had the following physical characteristics:

Refractive index (25°C,D)	1.573
Kinetic Viscosity (25°C)	1210 centistokes
Temperature-Viscosity coefficient	0,898
Volume resistivity (20°C)	2.8×10^{15} (OHM.CM)
Dielectric constant (20°C)	2.82
Dielectric dissipation factor (20°C)	7×10^{-5}
Surface tension	25,7 (Dyne/Square centimeter)
Coefficient of Friction (25°C)	0.15

Comparative Example 2

30.0 g (300 millimol) of dichlorosilane, 56.5 g (543 millimol) of styrene and 50 mol of an isopropanol solution of chloroplatinic acid ($H_2PtCl_6.6H_2O$) containing 4.83×10^{-6}mol of the acid were charged into a 200 ml pressure-proof stainless steel reaction tube and reaction was carried out as in the procedure of Example 3 by heating in an oil bath at 50°C for 15 hours with stirring. After reaction, the reacted liquid resinified and no diphenethyldichlorosilane could be obtained.

Comparative Example 3

31.7 g (314 millimol) of dichlorosilane, 56.3 g (541 millimol) of styrene and 0.2182 g (2.36×10^{-4} mol) of chlorotris(triphenylphosphine)rhodium(I) were charged into a 200 ml pressure-proof stainless steel reaction tube as in the procedure of Example 3 and reaction was carried out by heating in an oil bath at 150°C for 20 hours with stirring.

After reaction, the reacted liquid was distilled under a reduced pressure. 45.7 g (223 millimol) of a product found to be monophenethyldichlorosilane was obtained, but no diphenethyldichlorosilane was identified in the distillate.

Example 5

Following the procedure of Example 3, 73.2 g (725 millimol) of dichlorosilane, and 92.7 g (890 millimol) of styrene were reacted in the presence of 0.1164 g (1.68 x 10^{-4} mol) of chlorotris(triphenylphosphine) rhodium (I) at 100°C for 16 hours and then the reacted liquid was distilled to obtain 147.6 g of monophenethyldichlorosilane (b.p. 95°C/7 mmHg).

10.3 g (50 millimol) of the monophenethyldichlorosilane. 22.7 g (218 millimol) of styrene and 0.08 g (6.42 x 10^{-5} mol) of tetrakis(triphenylphosphine)platinum(0) were charged into a 100 ml stainless steel reaction tube and reacted by heating in an oil bath at 100°C for 15 hours with stirring. After reaction, the reacted liquid was distilled under reduced pressure to obtain 13.6 g of a product having a boiling point of 141°C/1.5mmHg and having the same ir, nmr and mass spectra as the product of Example 4. It was thus confirmed that the product produced by the present example was diphenethyldichlorosilane.

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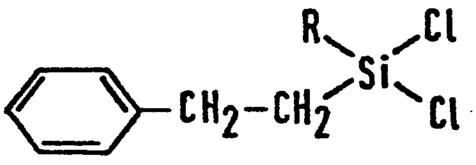
WHAT IS CLAIM IS:-

1. A substituted phenethyldichlorosilane having the general formula



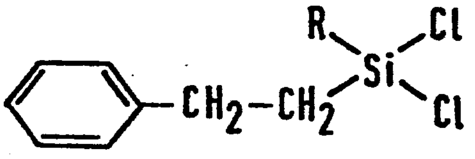
(1)

wherein R is an alkyl group having 3 to 20 carbon atoms or a phenethyl group.

2. A substituted phenethyldichlorosilane according to Claim 1 wherein R is an alkyl group having 3 to 20 carbon atoms.

3. A substituted phenethyldichlorosilane according to Claim 1 wherein R^3 is a phenethyl group.

4. A method for producing a substituted phenethyldichlorosilane having the general formula



(1)

wherein R is an alkyl having 3 to 20 carbon atoms or a phenethyl group, which comprises reacting at a temperature of 30 to 200°C a monosubstituted dichlorosilane having the general formula $RHSiCl_2$, where R is as defined, with styrene in the presence of a complex of platinum and a phosphine.

5. A method according to Claim 4 wherein the complex is tetrakis(triphenylphosphine)platinum(0).

6. A method according to Claim 4 or Claim 5 wherein R is an alkyl group having 3 to 20 carbon atoms and the reaction with styrene is effected at 30 to 110°C.

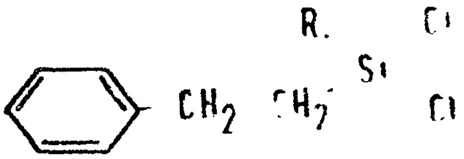
7. A method according to Claim 4 or Claim 5 wherein R is phenethyl.

8. A method according to any one of Claims 4 to 7 wherein the monosubstituted dichlorosilane $RHSiCl_2$ is prepared by reacting at a temperature of 30 to [illegible] dichlorosilane itself with, as may be appropriate, an α-olefin having 3 to 20 carbon atoms or styrene, in the presence of a complex of platinum and a phosphine.

9. A method according to Claim 8 wherein the complex employed for reaction of the dichlorosilane itself is also employed for reaction of the monosubstituted dichlorosilane produced.

10. A method according to Claim 9 wherein when R is phenethyldichlorosilane itself is reacted with 2 or more molar equivalents of styrene to give diphenethyldichlorosilane.

11. A method for producing a polysiloxane in which a dichlorosilane is hydrolysed and polymerised, wherein the dichlorosilane is a substituted phenethyldichlorosilane having the general formula



$$C_6H_5CH_2CH_2Si(R)Cl_2 \qquad (1)$$

BAD ORIGINAL

wherein R is an alkyl group having 3 to 20 carbon atoms or a phenethyl group.

FIG. 1

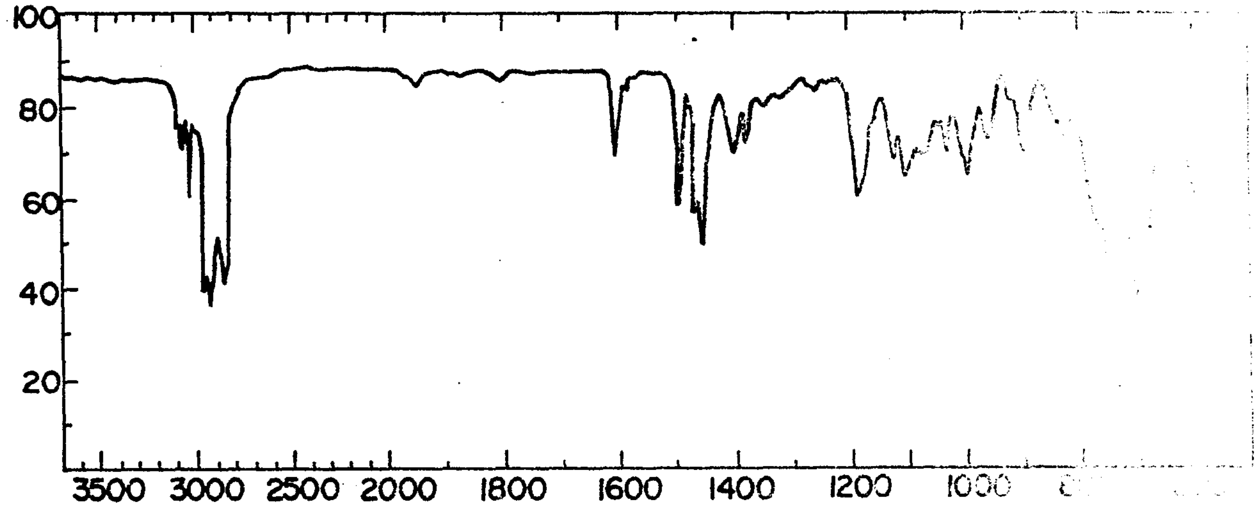

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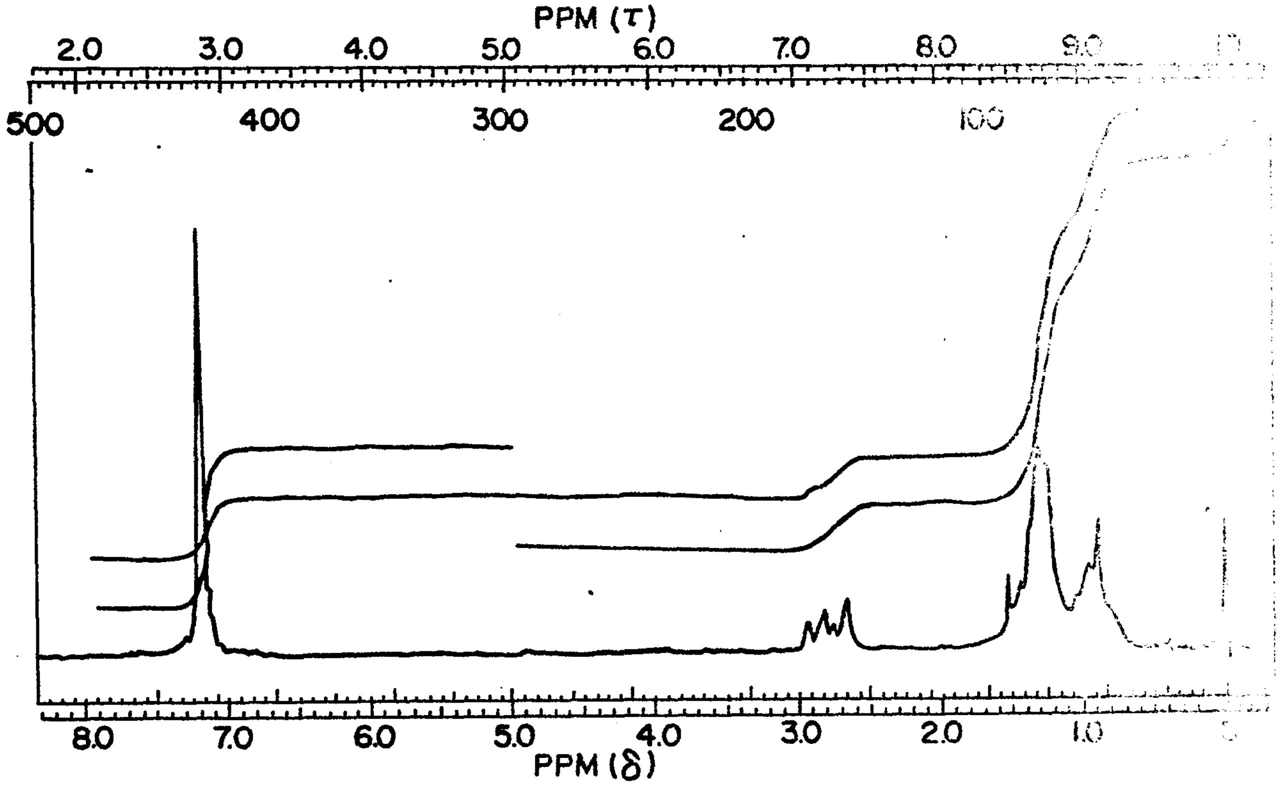
FIG. 2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PPM (δ)

FIG. 3

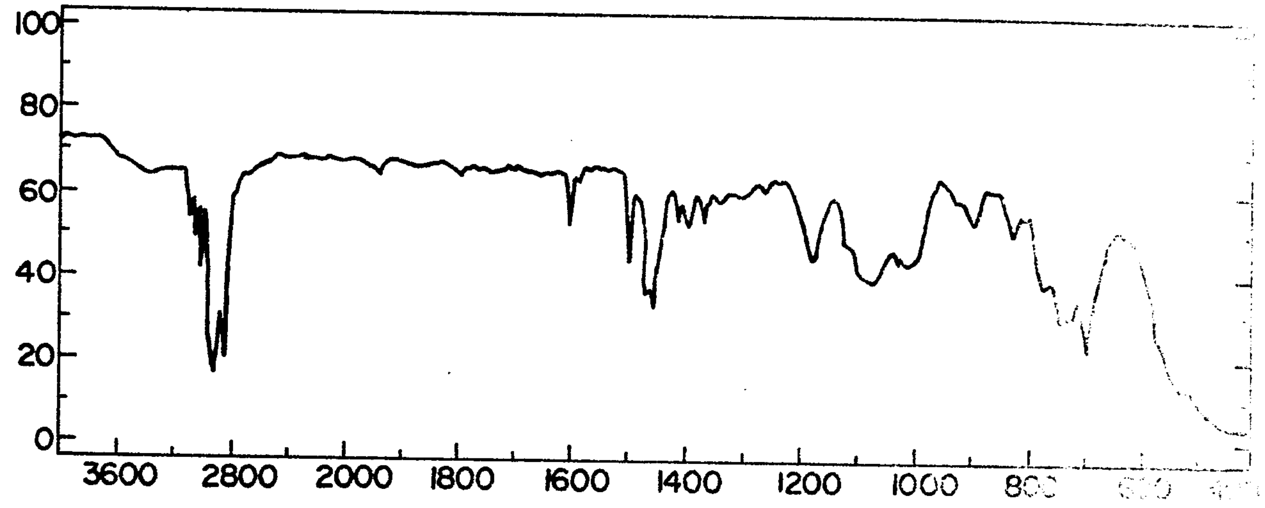
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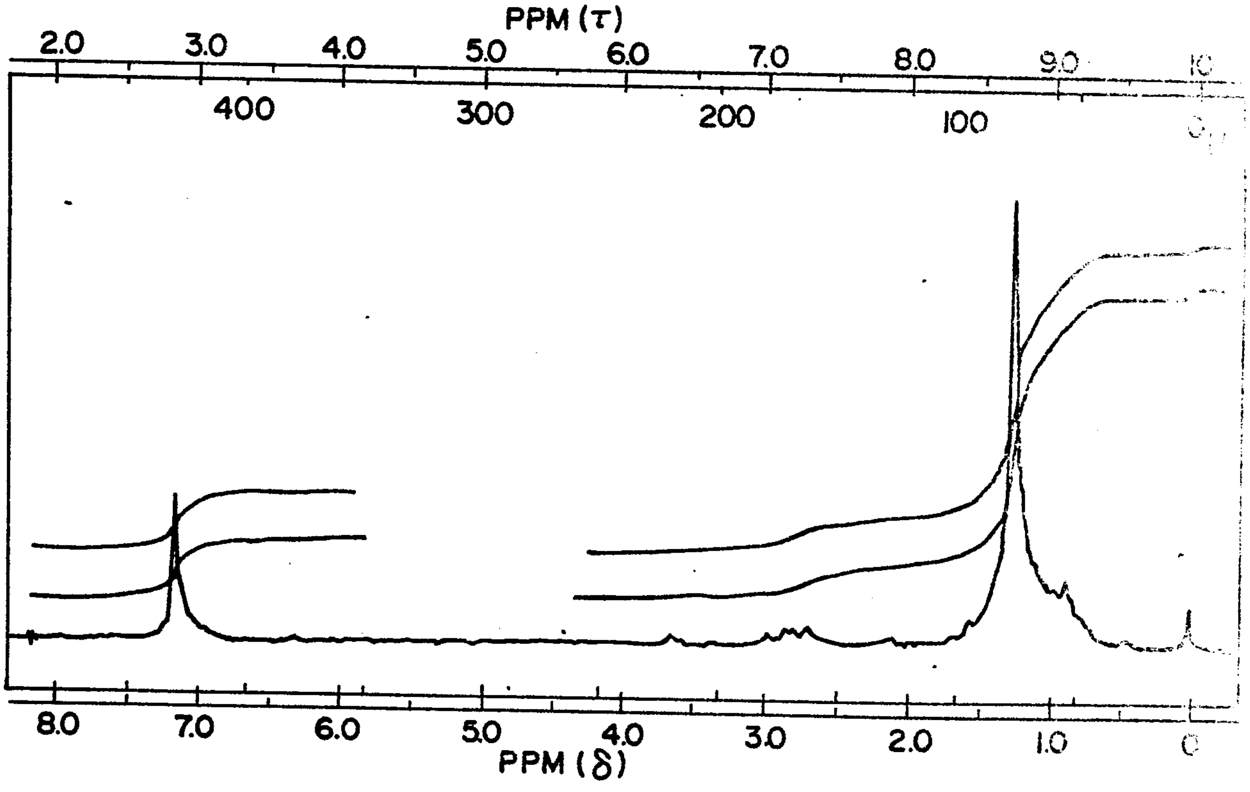
FIG. 4


PPM (τ)
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PPM (δ)

FIG. 5

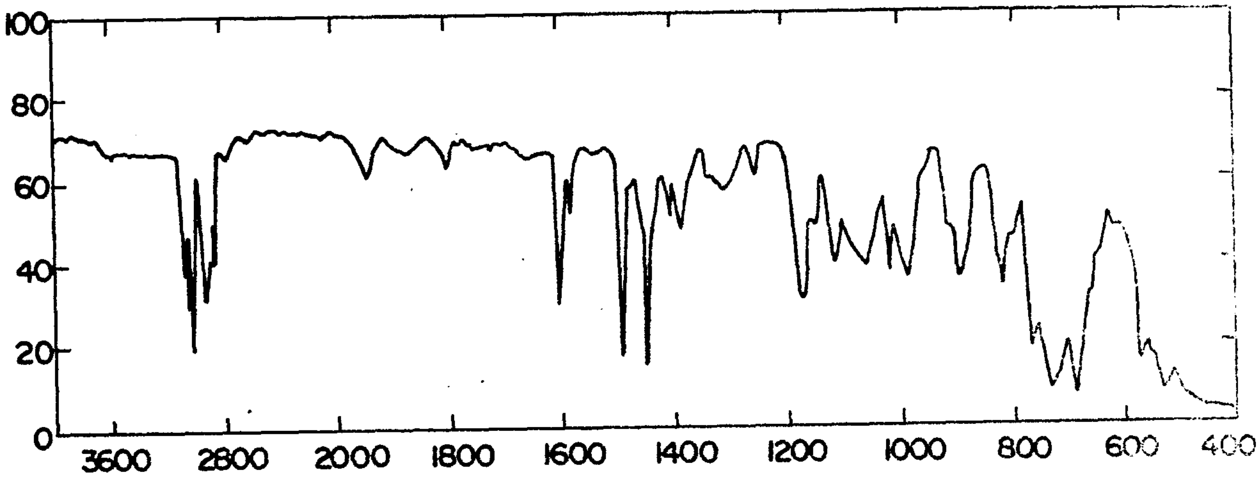
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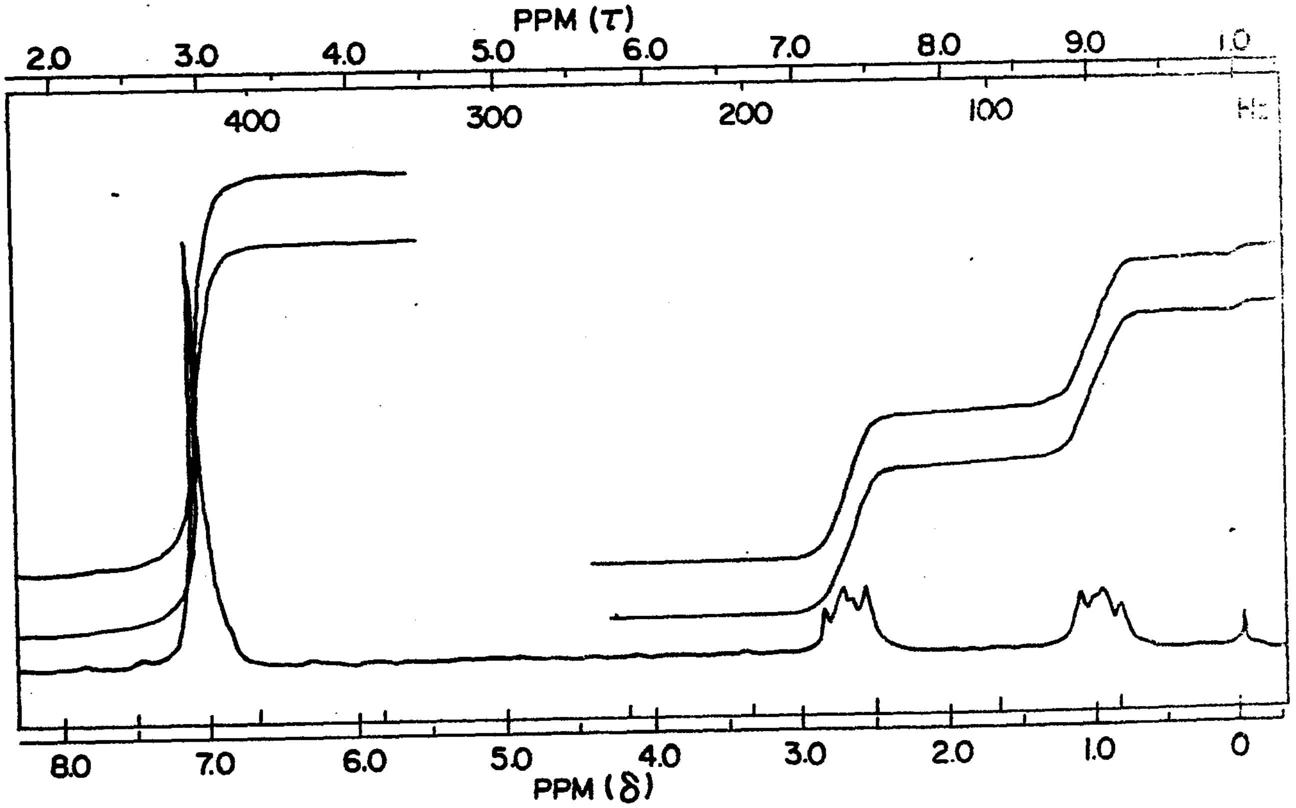
FIG. 6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2.0
1.0
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PPM (δ)

European Patent Office

EUROPEAN SEARCH REPORT

0000614

Application number

EP 78 30 0045

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	FR - A - 951 224 (DOW CORNING CORP.) * Page 2, lines 37-8,52; page 4, line 90 - page 5, line 9 * --	1-8
	FR - A - 1 169 051 (UNION CARBIDE) * Page 6, reaction (B); page 7, reaction (B) or table VII; abstract 1,2a-c * --	1-8
	US - A - 2 954 390 (ROSCOE A.PIKE et al.) * Column 2, lines 16-25, 35-38; column 7, lines 29-38 * --	1-8
	DE - B - 1 942 798 (TORAY IND.) * Column 21-22; claims 1,2; column 11, examples 71,72; column 15; example 115 * ----	4-10

CLASSIFICATION OF THE APPLICATION (Int Cl.²)

C 07 F 7/12

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

C 07 F 7/12

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search raport has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	07-09-1978	SUTER

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