



CHEMICAL AIDS IN DISTILLATION PROBLEMS

Monsanto Technical Data Sheet
Monsanto Chemical Company, Organic Chemicals Division, St. Louis 1, Mo.

February 26, 1954

AROCLORS*, HB-40*, HB-20*, PHENYLCYCLOHEXANE, BICYCLOHEXYL

All of the above materials are Monsanto chemicals which can be of value in certain distillation problems. These materials are high boiling solvents possessing good heat stability. The *AROCLORS* (a series of chlorinated polyphenyls) are especially noted for their chemical inertness. The other chemicals may also serve as inert solvents. Consequently, these materials all find use as distillation aids where the lower boiling material is subject to decomposition from localized overheating, and in cases where distillation residues are resinous or solid materials which are difficult to clean out of the still pot. The Monsanto chemicals listed also find considerable application as inert media for many chemical reactions.

An example of the value of such distillation aids is a case where a product distilling at about 78°C. at 40 mm. Hg. was separated without fractionation from *AROCOLOR* 1242 which, at the same pressure, boils at 210°C. Another product boiling at 100°C. at 2 mm. Hg. required only moderate fractionation to separate it from *AROCOLOR* 1242 boiling at 135°C. (at 2 mm. Hg.).

Which material to use in a given situation can be determined from the table of properties which appears on the next page. When reduced pressures are involved, further data may be obtained upon request.

AROCOLOR products 1242, 1248, 1254 and 1260 are liquids with progressively increasing boiling points. These liquids act as a stable heel in the still and allow all of the desired end product to be recovered. In cases where the distillation residue normally tends to polymerize into gummy materials or to decompose into solids, the liquid *AROCOLOR* compounds can be used to keep the residue as a free-flowing fluid for easier removal. Also, by allowing better heat transfer in the fluid, excessive decomposition and product loss can be minimized.

* Reg. U.S. Pat. Off.

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In addition to the liquid *AROCLOR* products, Monsanto offers *AROCLOR* 5460, a resinous solid which has been used to plasticize solid still residues to facilitate removal. This resin cannot be recovered and is discarded with the residue. From 25% to 30% of *AROCLOR* 5460, based on total residue weight, will satisfactorily plasticize most such residues.

When used as distillation aids, the liquid *AROCLOR* compounds can be reused several times and either discarded or distilled to restore their original refined state.

Used as stable solvents for reactions conducted in an inert liquid phase, the liquid *AROCLOR* compounds perform very well. Here again, the liquids can usually be used several times before discarding or re-purifying.

The other chemicals listed are included to offer a wider choice of boiling points both at normal and at reduced pressures. The table below will help to choose the correct compound for your reaction or distillation situation. Your Monsanto representative will be glad to discuss specific problems and to provide or obtain other data needed.

(Values are Approximate)	Phenylcyclohexane	Bicyclohexyl	<i>AROCLOR</i> 1242	<i>AROCLOR</i> 1248	<i>AROCLOR</i> 1254	<i>AROCLOR</i> 1260	HB-40	HB-20
Distillation Range	239-244°C.	238-242°C.	325-360°C.	340-375°C.	365-390°C.	385-420°C.	340-396°C.	312-370°C.
Pour Point	2.5-5.5°C.	1-3°C.	minus 19°C.	minus 7°C.	10°C.	31°C.	minus 25°C.	minus 54°C.
Viscosity (SUS at 100°F.)	31.2	34.2	80-93	185-240	1800-2500	72-78 (at 210°F.)	144	55.7 <i>96</i>
Specific Gravity	0.938 at 25°/15.6°C.	0.988 at 25°/15.6°C.	1.380 at 25°/25°C.	1.445 at 25°/25°C.	1.538 at 25°/25°C.	1.620 at 25°/25°C.	1.004 at 25°/15°C.	0.971 at 25°/15°C.

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PHENYLCYCLOHEXANE
(Cyclohexylbenzene)
and
BICYCLOHEXYL (Dicyclohexyl)

MONSANTO

PHENYLCYCLOHEXANE
and
BICYCLOHEXYL

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Phenylcyclohexane and bicyclohexyl are high boiling, colorless, oily liquids, free from objectionable odor and relatively free from toxicity.

Structurally, phenylcyclohexane is composed of one aromatic six membered carbon ring and one aliphatic (hydrogenated) six membered carbon ring.

Bicyclohexyl is composed of two aliphatic six membered carbon rings (both saturated with hydrogen).

Both products are suggested for use as high boiling solvents and compatibilizing agents and penetrating agents.

Interesting derivatives can be made from phenylcyclohexane by sulfonation, nitration, halogenation and condensation with reactive chemical agents.

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PHENYLCYCLOHEXANE (Cyclohexylbenzene)

Phenylcyclohexane is a product of hydrogenation of biphenyl under proper conditions to saturate one of the benzene rings.

Therefore, phenylcyclohexane possesses the properties of both aromatic and aliphatic nature.

It is a high boiling, colorless, oily liquid, free from objectionable odor and relatively free from toxicity.

Phenylcyclohexane is of interest as a high boiling solvent and compatibilizing agent and penetrating agent.

It possesses good electrical resistance, and interesting derivatives can be made from it.

The physical, electrical and chemical properties of phenylcyclohexane are described as follows:

PHYSICAL PROPERTIES

Molecular Weight:	160.25
Appearance:	Colorless Oily Liquid
Color:	Water White
Odor:	Pleasant
Specific Gravity (11)	0.938 $\pm$ 0.002 at 25/15.6°C.
Pounds per Gallon (11)	7.82 (Av.)
Refractive Index (11)	1.523 $\pm$ 0.002 at 25°C.
Viscosity (11)	31.2 Saybolt Seconds at 100°F.
Freezing Point (11)	2.5-5.5°C.
Distillation Range (11)	239 -- 244°C.
5% to 95%	210°F.
Flash Point, open cup (11)	220°F.
Flame Point, open cup (11)	
Vapor Pressure (11) (12)	

Temperature, °C.	Pressure, mm.Hg.
20	0.1
30	0.15
40	0.30
50	0.60
70	2.0
100	9.0
136.65	40.0
163.6	100.0
186.25	200.0
221.7	500.0
240.1	760.0.

Electrical Properties — Typical Values (11)

Dielectric Constant at 25°C. — 60 cycles to 100 kc	— 2.54
Dielectric Constant at 100°C. — 60 cycles to 100 kc	— 2.45
Power Factor at 100°C. — 60 cycles	— 0.22%
Volume Resistivity at 100°C., 500 volts DC	— 50,000 $\times$ 10 ⁹ ohm-cm.

COMPATIBILITY OF PHENYLCYCLOHEXANE (III)

Phenylcyclohexane is not soluble in water, but is miscible at 25°C. with many solvents and oils of which the following are typical:

Solvent	Solubility
Acetone	Miscible
Benzene	Miscible
Carbon Tetrachloride	Miscible
Castor Oil	Miscible
Dichloromethane	Miscible
Ethyl Acetate	Miscible
Ethyl Alcohol	44 ml. of phenylcyclohexane will dissolve in 100 ml. of alcohol at 25°C.
Glycerine	Immiscible
Hexane	Miscible
Mineral Oil	Miscible
Stoddard Solvent	Miscible
Trichlorobenzene	Miscible
Xylene	Miscible

SOLUBILITY OF SOME ORGANIC COMPOUNDS IN PHENYLCYCLOHEXANE AT 25°C. (III)

Solute	Grams/100 Gms. Phenylcyclohexane
Biphenyl	55
DDT	53
Naphthalene	38
Paraffin Wax	18
Stearic Acid	13
Pentachlorophenol	4.7
Santowax O	69
Santowax M	14
Santowax P	3.4
Santowax R	3.3

CHEMICAL PROPERTIES

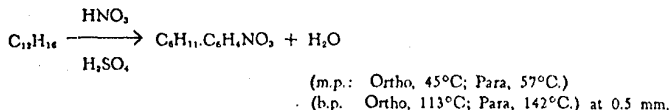
p Cyclohexylbenzene Sulfonic Acid

Phenylcyclohexane can be readily sulfonated with 100% H_2SO_4 (9). The barium, sodium, potassium, lead and nickel salts of the sulfonic acid have been prepared (6).



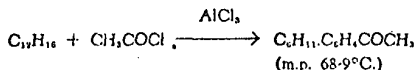
Nitro Cyclohexylbenzene

A mixture of ortho and para nitrocyclohexylbenzene can be prepared by nitration with HNO_3 and acetic acid (7), HNO_3 and acetic anhydride (10), and fuming HNO_3 and H_2SO_4 (6). The para isomer predominates. The corresponding amines can be readily obtained by reduction of the nitro compounds.



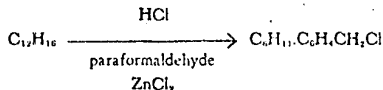
p-Cyclohexylacetophenone

The ketone derivative is obtained by condensing acetyl chloride (7) (8) or acetic anhydride (4) with phenylcyclohexane in the presence of aluminum chloride.



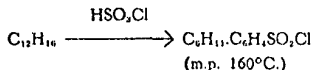
Chloromethyl Cyclohexylbenzene

The chloromethyl derivative of phenylcyclohexane has been made by reaction with paraformaldehyde, zinc chloride and HCl (1) (2) (3).



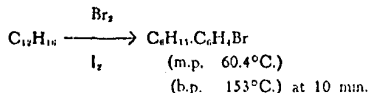
p-Cyclohexylbenzene Sulfonyl Chloride

With chlorosulfonic acid, phenylcyclohexane forms paracyclohexylbenzene sulfonyl chloride in yields of 85% (5).



p-Bromocyclohexylbenzene

In an excess of phenylcyclohexane with an iodine catalyst bromination proceeds to the p-bromo derivative (1) (13). The bromide forms the Grignard reagent.



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(See next page for BICYCLOHEXYL)

BICYCLOHEXYL (Dicyclohexyl)

Bicyclohexyl is a product of the hydrogenation of biphenyl under proper conditions to saturate both aromatic rings. The material is a colorless oil possessing a pleasant odor. It is relatively non-toxic to higher animals.

U. S. Patent 2,448,093 L. D. Gittings) includes dicyclohexyl as an ingredient in penetrating oil. Military Specifications MIL-F-7197 lists dicyclohexyl as a rubber swelling reference fluid (1).

PHYSICAL PROPERTIES

Molecular Weight	166.30
Appearance	Clear, mobile liquid
Color	Water white
Odor	Pleasant
Specific Gravity (2)	0.883 $\pm$ 0.002 at 25/15.6°C.
Pounds per Gallon (2)	7.37 (Average)
Refractive Index (1) (2)	1.4800 $\pm$ 0.002 at 20°C.
Viscosity (2)	34.2 Saybolt Seconds at 100°F
(3) (4)	3.07 Centistokes at 100°F
(3) (4)	1.23 Centistokes at 210°F
Freezing Point (2)	-4.3°C.
Distillation Range (2) 5% to 95%	238-242°C.
Flash Point, open cup (2)	215°F.
Flame Point, open cup (2)	220°F.
Aniline Point, °C. (2) (3)	48.2°C.
Vapor Pressure (2) (5)	

Temperature, °C.

20
30
40
50
60
70
100
134.35
161.2
184.45
220.15
238.5

Pressure, mm Hg.

0.1
0.2
0.4
0.8
2.5
10.5
40
100
200
500
760

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