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REMOVAL OF TROUBLESOME FRACTIONS FROM BENZENE HEXACHLORIDE

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This invention relates to a method for removing from benzene hexachlorides certain materials, commonly present therein, which cause trouble in the separation of the economically important gamma-isomer thereof. It relates in particular to a method of removing the delta-isomer of benzene hexachloride from mixtures of the other isomers of that compound, and for removing hepta-chloro- and octa-chlorocyclohexanes from benzene hexachloride mixtures containing them.

It is known that benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) occurs in a number of isomeric forms, that these isomers are produced together in varying amounts by the addition chlorination of benzene, that the gamma-isomer is the active insecticidal constituent of such mixtures, and that it is difficult to separate the isomers completely from one another. It has been recognized, also, that certain small amounts of hepta-chloro- and even octa-chlorocyclohexane may be, and commonly are formed with and present in the mixed benzene hexachlorides so-produced. Data are available showing the solubility of each of the isomers of benzene hexachloride in each of numerous common solvents, but these data have no significance when dealing with mixtures of the various isomers, especially when the delta-isomer and the hepta- and octa-chlorocyclohexanes are present. This is due to the surprisingly high activity of these compounds as co-solvents for the isomeric forms of benzene hexachloride. Thus, when these troublesome factors are present, the only generalization from the solubility data derived from work on pure isomers which holds true is that the beta-isomer is relatively insoluble. When the named troublesome factors are present, many liquids which would only dissolve significant amounts of one or two of the pure isomers become capable of dissolving nearly all of the isomers and in proportions which are unpredictably at variance with their behavior toward the pure isomers.

The gamma-isomer of benzene hexachloride is an active insecticidal agent, while the other isomers of this compound show little, if any, insecticidal activity. The gamma-isomer and the delta-isomer are readily soluble in a variety of solvents when in the pure state, and separation of the gamma-isomer from other isomers by selective extraction is made practically impossible when the mixture containing it also contains significant amounts of the delta-isomer of benzene hexachloride, as well as when such mixture contains hepta- and octa-chlorocyclohexanes. These factors make it difficult to attain the desired end of producing a benzene hexachloride product having much more than the normal amount of the gamma-isomer which is originally produced as 10 to 12 per cent of the product of the most common process, and 14 to 18 per cent in certain improved processes. It is still desirable to provide a simple method whereby the concentration of gamma-isomer may be increased to the range of 30 to 60 per cent, or more, and the product may be obtained as a dry, non-tacky crystal free from the aforesaid troublesome fractions.

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It is the principal object of the present invention to provide a method whereby isomeric mixtures of benzene hexachlorides may be freed from the delta-isomer of that compound and from hepta-chlorocyclohexane and octa-chlorocyclohexane present therein as impurities. A related object is to provide such a method whereby there may be obtained a dry, non-tacky benzene hexachloride, enriched as to its gamma-isomer content to values in the range from 30 to 60 per cent, or more, and free from the said troublesome fractions. Other and related objects may appear hereinafter. In the following description, the term "crude" is applied to the benzene hexachloride mixture obtained by addition of chlorine to benzene.

I have discovered one manner in which the foregoing objects may be attained. In accordance with this invention, the crude product obtained by the addition chlorination of benzene, after first being recovered in solid form from the reaction medium, is thoroughly mixed with an amount of an organic solvent for the gamma-isomer of benzene hexachloride only sufficient to retain in solution at room temperature from 30 to 60 per cent of the weight of the mixture being treated; heating the slurry of crude chlorinated product and solvent to a temperature which encourages solution, suitably from 45° to 100° C., but not above the boiling point of the solvent at the pressure employed; then cooling the mixture, with stirring, to 25° C. or cooler until equilibrium between solid and liquid phases is reached; and filtering the solution from the solids. The filtrate, containing most of the gamma-isomer and substantially all of the defined troublesome factors, is freed from solvent, leaving a sticky solid mass normally exhibiting a strong odor due to the impurities present. This mass is mixed with 60 to 75 per cent of its weight of 2-propanol and is first heat-

ed to a temperature up to the boiling point (82° C.) of 2-propanol, and preferably to about 70° C., then cooled, with stirring, to about 10° to 20° C., and the resulting crystals are recovered by filtration. These crystals are found to contain much less hepta- and octa-chlorocyclohexane and delta-isomer of benzene hexachloride, and to be substantially free from objectionable odor commonly associated with benzene hexachloride. They are retreated in the same manner with 2-propanol, to yield crystals free from the troublesome fraction and containing a concentration of from 30 to 60 per cent of gamma-benzene hexachloride, the balance being mostly the alpha-isomer with no more than traces of the delta-isomer. When air-dried to remove 2-propanol, the material which had been crystallized from that medium is found to be a non-tacky, free-flowing white crystalline product.

The preferred solvent for use in the first stage of the process, in which the gamma- and delta-isomers are both extracted from the crude reaction product, is propylene chloride, though any of several other solvents may be used if care is taken not to dissolve more than 60 nor less than 30 per cent of the original mixture in such solvent. Examples of other solvents are ethylene chloride, chloroform, acetone, benzene, monochlorobenzene, trichloroethylene, toluene and xylene.

2-propanol is the only solvent which has been found capable of converting a benzene hexachloride mixture rich in both gamma- and delta-isomers and in hepta- and octa-chlorocyclohexanes to a useful, non-sticky and substantially odorless, free-flowing crystalline product free from the identified troublesome fractions. It is, accordingly, the material used in the second stage of the present process.

The following example illustrates the practice of the invention:

Benzene hexachloride was obtained by photochlorination of benzene, and had the following approximate analysis:

	Per cent
alpha	66
beta	8
gamma	12
delta	6
epsilon	3
hepta- and octa-chlorocyclohexanes (by difference)	5

2000 pounds of this product was mixed with 2000 pounds of propylene chloride, and the mixture was heated to 80° C., and cooled, while being thoroughly agitated, to 20° C. The resulting slurry was filtered, and the filter cake was washed with a small additional amount of propylene chloride which was added to the filtrate. The filter cake, when air dried, weighed 1250 pounds, and, according to infra-red analysis, consisted of:

	Per cent
alpha	80
beta	12.5
gamma	2
delta	not over 1
epsilon	about 1

The filtrate, containing about 750 pounds of mixed solids dissolved in propylene chloride, was steam distilled to remove the solvent, and the resulting sticky mass was freed from most of the adherent water by centrifugal action. The remaining organic solids contained about 45 per cent alpha-isomer and about 30 per cent gamma-isomer, and the balance was largely the

delta- and epsilon-isomers of benzene hexachloride together with hepta- and higher chlorocyclohexanes.

About 700 pounds of this sticky material was stirred into 460 pounds of 2-propanol, and the mixture was heated to 70° C. and then cooled, while stirring, to 15° C. The deposited crystals were recovered by filtration, and were treated a second time and in the same manner with about 70 per cent of their weight of 2-propanol. The crystals deposited from this treatment were recovered, air-dried to remove excess 2-propanol, and were found to weigh 382 pounds. This product was white, free-flowing, and substantially free from irritating odors. It contained approximately

	Per cent
alpha	44
beta	none
gamma	49
delta	1
epsilon	3

These purified crystals contained 78 per cent of the gamma-isomer of benzene hexachloride which was present in the 2000 pounds of crude material originally fed to the process. The 2-propanol filtrate contained over 300 pounds of mixed isomers and impurities, including about 85 per cent of the original delta-isomer and 60 per cent of the original epsilon-isomer of benzene hexachloride, and substantially all of the more highly chlorinated impurities.

It has been found in the 2-propanol purification of benzene hexachloride that, when less than about 70 per cent as much 2-propanol as benzene hexachloride is used, the solid product obtained is proportionately richer in impurities and leaner in gamma-isomer, while the use of much larger ratios of 2-propanol to benzene hexachloride both reduces the yield of the improved product and gives that product a lower concentration of the gamma-isomer. The practical operating ratio of 2-propanol to benzene hexachloride is in the range of 60 to 75 per cent, by weight in each treatment. This process produces its desired result only when applied to a mixture of benzene hexachloride isomers which has been enriched by prior treatment to contain from 20 to 30 per cent, or more, of the gamma-isomer and which contains, as well, some or all of the troublesome fractions previously defined. The 2-propanol employed in the present process may be, and preferably is anhydrous, but it may contain up to about 10 per cent of water, without altering its effectiveness in the described separation.

The process is useful, not only for the increased insecticidal value and low odor level of the product obtained, but also because the so-purified and enriched product provides a perfect feed for further selective solvent treatment to recover substantially pure gamma-benzene hexachloride. One such treatment is described in my concurrently filed application, Serial No. 51,864, and, in a preferred embodiment, consists essentially in mixing the product of the present invention with about 1.5 times its weight of chloroform at room temperature, separating the resulting solution from residual solids, heating the solution to about 60° C., cooling the solution in a quiescent condition to from 10° to −10° C., and recovering the deposited crystals of gamma-benzene hexachloride having a purity commonly over 95 per cent. If the latter product is recrystallized from carbon tetrachloride, for example, there may be ob-

tained gamma-benzene hexachloride of purity over 99 per cent, in an amount approaching half of that originally present in the crude product obtained by chlorinating benzene. As pointed out in my said concurrently filed application, the material produced by the present invention may be treated as above-outlined using chloroform, or ethyl ether, or monochlorobenzene, or other good gamma-isomer solvent, to obtain the gamma-isomer with a purity of over 90 per cent, and that, in each case, better yields of purified gamma-isomer are obtained when the solvent employed is practically saturated with respect to the alpha-isomer when it is passed through the solids from which it picks up the gamma-isomer, prior to crystallization of the latter in purified form.

I claim:

1. The method which comprises mixing crude solid benzene hexachloride, containing less than 30 per cent of the gamma-isomer thereof, with an amount of an organic solvent for the gamma-isomer of benzene hexachloride, selected from the group consisting of acetone, chloroform, ethylene chloride, trichloroethylene, propylene chloride, benzene, monochlorobenzene, toluene and xylene, which is sufficient to retain in solution at room temperature only 30 to 60 per cent of the weight of the crude benzene hexachloride being treated; heating the resultant slurry to a temperature from 45° to 100° C., but below the boiling point of the solvent employed; cooling the mixture at least to 25° C. until equilibrium is reached; separating the solution from undissolved solids; recovering from the solution the solute which comprises most of the troublesome fractions including the delta-benzene hexachloride and the hepta- and higher chlorocyclohexanes which were in the original crude mixture; mixing the so-recovered solute with from 60 to 75 per cent of its weight of 2-propanol to form a slurry; heating the slurry to a temperature up to the boiling point of 2-propanol; cooling this slurry, with stirring, to from 10° to 20° C.; recovering the undissolved crystals of benzene hexachloride in a state of improved purity; treating these crystals again in like manner with 2-propanol and recovering crystals characterized by a gamma-isomer content from 30 to 60 per cent and by substantial freedom from said troublesome fractions.

2. The method which comprises mixing crude solid benzene hexachloride, containing less than 30 per cent of the gamma-isomer thereof, with an amount of propylene chloride which is sufficient to retain in solution at room temperatre only 30 to 60 per cent of the weight of the crude benzene hexachloride being treated; heating the resultant slurry to a temperature from 45° C. to the boiling point of propylene chloride; cooling the mixture at least to 25° C. until equilibrium is reached; separating the solution from undissolved solids; recovering from the solution the solute which comprises most of the troublesome fractions including the delta-benzene hexachloride and the hepta- and higher chlorocyclohexanes which were in the original crude mixture; mixing the so-recovered solute with from 60 to 75 per cent of its weight of 2-propanol to form a slurry; heating the slurry to a temperature up to the boiling point of 2-propanol; cooling this slurry, with stirring, to from 10° to 20° C.; recovering the undissolved crystals of benzene hexachloride in a state of improved purity; treating these crystals again in like manner with 2-propanol and recovering crystals characterized by a gamma-isomer content from 30 to 60 per cent and by substantial freedom from said troublesome fractions.

3. The method of refining a benzene hexachloride product containing at least 20 and not as much as 60 per cent of gamma-benzene hexachloride together with 10 to 30 per cent, in the aggregate, of troublesome fractions including delta-benzene hexachloride and hepta- and higher chlorocyclohexanes, substantially all of the balance being alpha-benzene hexachloride, which comprises mixing such a material with from 60 to 75 per cent of its weight of 2-propanol to form a slurry; heating the slurry to a temperature up to the boiling point of 2-propanol; cooling this slurry, with stirring, to from 10° to 20° C.; recovering the undissolved crystals of benzene hexachloride in a state of improved purity; treating these crystals again in like manner with 2-propanol and recovering crystals characterized by a higher gamma-isomer content which is from 30 to 60 per cent and by substantial freedom from said troublesome fractions.

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