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PROCESS OF MAKING CHLORINATED BODIES.

No Drawing.

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To all whom it may concern:

Be it known that we, CARLETON ELLIS and ALFRED A. WELLS, citizens of the United States, and residents of Montclair, in the county of Essex and State of New Jersey, have invented new and useful Improvements in Processes of Making Chlorinated Bodies, of which the following is a specification.

This invention relates to a method of producing halogenated (e. g. chlorinated) products from olefins or other unsaturated bodies of an analogous character present in or derived from petroleum material and the like.

The raw material suitable for carrying out the present process may be found in large quantities in cracked gasoline or in the still gases or vapors from cracking stills and other operations employed in the petroleum industry. A form of cracked gasoline which is suitable for the present process is so-called Burton oil made by cracking heavy petroleum residues under a pressure of 75 lbs. or so. The lighter fractions boiling up to say 110–120° C. contain perhaps 10 to 20% of unsaturated bodies, a considerable portion of which are olefins adapted for use in the present process. These olefins may be extracted by treatment with sulphuric acid and halogenated to form the products described herein. In like manner other cracked products both light and heavy, depending upon the particular halogen product desired may be used. Olefins obtained from other sources such as the natural olefins of shale oil or mineral oils of other kinds, also olefins obtained in various operations such as the production of Pinsch gas, Blau gas and the like or regenerated olefins obtained in the sulphation process of making alcohols or other olefin material may be likewise employed. When products of comparatively low molecular weight are desired it is possible to utilize the "still gases" from petroleum which contain the vapors of unsaturated bodies. Gases obtained by cracking petroleum in stills or in tubes may be collected and absorbed in sulphuric acid to give an acid extract suitable for making chlorinated or other form of halogenated bodies. In employing moist still gases it is important to dry these so that the sulphuric acid will not be diluted to a point where it will fail to absorb the gases freely.

The acid preferably employed as indicated from the foregoing is sulphuric acid, but any similarly acting acid may be used; especially one of a dibasic or polybasic character. Mixtures of selenic acid or phosphoric acid with sulfuric acid may be used, for example. Use of sulfuric acid is described herein. One difficulty which has heretofore been an obstacle in producing pure or fairly pure derivatives of petroleum has been to secure a proper fraction of the petroleum of the desired purity having the necessary reactive qualities. In a product as complex as gasoline, for example Burton oil distillates, when a reaction produces products which are miscible in the gasoline, great difficulty would arise in their separation by distillation or other methods. In the present case the sulphuric acid compound or product formed which is herein termed acid extract or acid concentrate, separates with the greatest ease from the gasoline material so that simple settling or centrifuging enables the olefin acid extract to be obtained in a state of comparatively high purity almost wholly free from the great bulk of saturated hydrocarbon in which the olefins were initially dissolved or associated. Such a procedure thus enables a pure product, that is to say a product consisting mainly of olefins and sulphuric acid or the products of the reaction of the acid on the olefins to be isolated in condition where it may be further treated for the production of chlorine-containing organic bodies. Likewise saturated hydrocarbons are isolated and may be used in the arts where unsaturated hydrocarbons would be objectionable.

The production of the acid extract is an operation requiring considerable care in order to utilize the olefin material to good advantage. Some olefins readily polymerize in the presence of strong sulphuric acid producing hydrocarbons, tars, resins and the like, which generally speaking are useless for the present purpose. While ethylene is quite stable in contact with strong sulphuric acid, and in fact apparently forms a compound therewith which is stable even when heated, the higher olefins polymerize or form tars quite quickly with strong sulphuric acid especially when the temperature is somewhat elevated. Accordingly in absorbing ethylene from still gases and the

like the sulphuric acid may be heated and it may be strong, as for example 66° B. or 98% acid or even fuming acid. In handling still gases the higher olefins may be dissolved in diluted acid kept cool during the operation, as for example by vigorously agitating a quantity of sulphuric acid of 1.8 specific gravity kept at a temperature between 10 and 20° C. while the acid is churned in contact with the gas, or by bubbling the gas therethrough. Under these conditions very little ethylene is dissolved and the gases leaving the first extractor may be passed into a second extractor where there is present acid of 1.84 sp. gr. or higher and heated to 50 or 100° C. more or less. In this extractor the ethylene is absorbed to a considerable extent at least and the issuing gases largely depleted of their unsaturated material may be burned as fuel or used in other ways. Being largely freed of saturated bodies under normal conditions of operation, the saturated bodies may be used in various ways where saturated products are required. The acid extract in the first extractor is collected separately from that in the second extractor so as to be chlorinated separately and thus the different chlorination products kept from being mixed; or alternately the extracts from the two extractors or series of extractors may be mixed and chlorinated. The still gases may be treated in other ways; as for example by passing through towers containing sulphuric acid operating on the counter-current system. In like manner the liquid gasoline obtained from cracking is agitated with the sulphuric acid, diluted acid or preferably acid of 1.8 specific gravity being run in a slow stream with cooling into a large body of gasoline while agitating violently and allowing to settle, and collecting the extract which forms a fairly clearly defined layer on the bottom after standing for a brief period. Or the gasoline may be run into the acid in some cases. If desired, the extract may be blown with air or exposed to a vacuum to withdraw any loosely bound or entrained volatile hydrocarbons.

We have found that it is possible to directly chlorinate the acid extract produced by the sulphation treatment of the olefins. This sulphated material or acid extract may be treated as a chemical entity and may be subjected to halogenation in various ways to produce chlor or brom compounds and the like.

While the process herein described directly involves the production of petroleum derivatives containing halogen and more particularly chlorinated bodies, the invention, in certain of its aspects, covers the process of isolating hydrocarbons as well. Gasoline made by the cracking process contains relatively large quantities of unsatur-

ated hydrocarbons. In ordinary refining processes it would not be feasible to take out these unsaturated bodies owing to great shrinkage losses and the cost of the large amount of sulphuric acid required. Consequently it is the practice to treat gasoline made in this way with sulphuric acid, say in a proportion of 3 to 5 lbs. acid per barrel of gasoline, the purpose of this treatment being to remove some of the very highly unsaturated bodies such as acetylene derivatives which give a strong odor to the product and which also tend to discolor it. Thus gasoline is placed on the market containing from 5% and upwards of unsaturated bodies and these often give trouble due to the fact that on exposure to the air some of the unsaturated bodies oxidize forming thick viscous compounds which are insoluble in the gasoline and separate causing considerable trouble. When this action takes place in the carburetor of a gas engine much trouble ensues. As an extraction agent for removing fatty oils from seed meal, etc., a saturated hydrocarbon solvent which does not leave a bad odor in the meal is desired. Unsaturated gasoline is not satisfactory for this purpose in many cases. In dry cleaning, cleaning gloves, etc., a saturated hydrocarbon solvent which leaves no bad odor in the goods is greatly desired. Unsaturated compounds often leave an objectionable and very persistent odor. According to the present process it is possible to use a great excess of sulphuric acid over what is ordinarily employed in refining and the unsaturated bodies may thus be largely or practically entirely removed if desired, furnishing on the one hand useful petroleum derivatives containing halogen and on the other hand yielding hydrocarbons which after refining may be said, from the standpoint of degree of saturation, to quite closely approach Pennsylvania gasoline, which has been the standard of high quality due to its being composed almost entirely of saturated bodies. In the present process therefore after the extraction with sulphuric acid the gasoline may be collected and washed to remove free sulphuric acid and sulphonic compounds, etc., alkali being employed for the purpose. Material containing 10-20% unsaturated bodies may have these reduced by the present process to but a small percentage or practically none whatever, giving a sweet mixture of hydrocarbons acceptable as an extraction solvent. Ordinarily we do not reduce the content of unsaturated bodies below 2 or 3% as the remaining olefins are relatively stable.

While in the foregoing we have mainly confined ourselves to olefins of a liquid character it should be distinctly understood that any olefin ranging from ethylene or propylene up through the series may be used in-

cluding various straight chain and branching chain olefins, cyclic unsaturated hydrocarbons and all the other unsaturated bodies produced in cracking petroleum which react with sulphuric acid or other separating agent and chlorination vehicle to enable the present process to be carried out.

In one case a concentrated extract was made by saturating sulphuric acid of about 1.8 specific gravity with olefin material (B. P. 35-45° C.) obtained from cracked petroleum. This was treated with chlorine gas until the increase in weight was fully one-half the weight of the olefin taken. The temperature was not allowed to rise above 35° C. and under these conditions the reaction took place readily but not violently. There was no separation of chlorinated hydrocarbons from this mixture. When diluted with water and distilled a liquid heavier than water and insoluble therein distilled over. This was separated from the water and a portion was distilled. The initial boiling point was 120° C. and about two-thirds of the entire quantity of the material distilled over between 120° C. and 170° C. No odor of hydrochloric acid was perceptible during the distillation. The product burned with a flame having a green fringe. A portion was boiled with strong caustic soda under a reflux condenser for one hour and after this treatment the material had an alcoholic odor, although still containing some chlorine. In like manner the brominated compound may be obtained by the addition of bromine to the acid extract or concentrate. Iodine containing bodies may be produced by combination with iodine.

In another case olefin material was incorporated with sulphuric acid to form alkyl hydrogen sulphate or a solution containing the olefin in a substantially non-polymerized state suitable as an acid extract or concentrate for chlorination purposes. The solution was diluted with water to render the strength of the sulphuric acid, if reckoned as such, approximately 70% and any saturated or unsaturated hydrocarbons insoluble in the diluted extract were removed. The solution was placed in a receptacle surrounded by cold water and chlorine was passed in until enough chlorine had been introduced in to produce a monochlor compound, calculating the mean molecular weight of the olefin material on the basis of 5 carbon atoms. The treatment with chlorine did not cause the acid concentrate to become heated to any material extent under these conditions. An equal volume of water was added and an immiscible layer separated, which was distilled. This layer contained most of the chlorinated material although a small amount was still left in the diluted acid ex-

tract and was obtained by distilling the latter. Products having the following characteristics were obtained:

	Sp. gr.	
Below 90°	.78	70
90-100	.876	
100-110	.89	
100-140	.949	

In like manner a bromine or other halogenated product may be produced either from acid extract or concentrate obtained from gasoline or by the use of mixtures of olefins containing little or no unsaturated hydrocarbons.

The third method of treatment is that of preparing the acid extract and adding a salt of a halogen as sodium chloride or a bromide or iodide. The sodium, potassium, calcium, barium or other salts may be used. In one case the olefin was dissolved in sulphuric acid and sodium chloride added, no reaction being noticed until the reaction liquid was heated to 30-35°. No odor of hydrochloric acid was detected but rather an odor of sulphur dioxide. A chlorinated hydrocarbon insoluble in water was obtained together with a certain amount of polymerized hydrocarbon. Sodium or calcium fluoride may be used in like manner to produce fluorine derivatives. The acid extract employed may be either concentrated or diluted when the salts are added. For an example with an olefin having one double bond the addition of, for example, sodium chloride, in an amount sufficient to furnish one molecular weight of hydrochloric acid to a molecular weight of olefin is a satisfactory proportion to employ. With acid extract of unsaturated olefine material averaging five carbon atoms and containing about 49 parts of sulfuric acid, about 29 parts of sodium chloride will give substantially this molecular relation, although greater or lesser amounts may be used if desired. The temperature should be regulated to keep the reaction liquid cool or at least not at a temperature at which objectionable polymerization takes place rapidly. As the degree or ease with which unsaturated hydrocarbons polymerize depends very largely on their structural character and molecular weight, the conditions may be duly adjusted with reference to the particular material in hand. In like manner hypochlorous acid or hypochlorites may be introduced into the acid extract. For example bleaching powder may be added to the acid extract with careful stirring and cooling to yield chlorinated compounds such as chlorhydrins and the like. In place of using salts such as sodium chloride, the free acid, such for example, as dry hydrochloric acid gas may be passed into the acid extract with agitation to bring about reaction.

Thus there are obtained simple chlorinated hydrocarbons as for example from ethylene by treatment with chlorine an ethylene dichloride may be obtained while
5 from propylene and butylene the corresponding chlorinated hydrocarbons are produced and thus from cracked gasoline new products are obtained, namely mixtures of chlorinated hydrocarbons ordinarily corresponding to the olefins of cracked gasoline
10 or of the unsaturated material of the particular raw hydrocarbons employed. Such correspondence is not wholly exact as some polymerization or other changes may occur; but in general it may be stated that this invention especially aims to produce from an acid extract made with say propylene butylene and amylene, a mixture of chlorinated propylene, butylene and amylene. In carrying out the reaction on a large scale the apparatus may be cooled by a cooling jacket or by pipes through which the water or brine is passed, at least during that stage when considerable heat is evolved.
25 The concentration or degree of dilution of the acid extract may vary considerably depending on whether or not chlor compounds such as chlorethane or dichlorethane, monochlor propane and the like are desired or whether chlorhydrins are to be produced as the more diluted the extract the greater the ease with which chlorhydrins may be expected to be formed, other conditions being equal. Thus the process comprises chlorinating unsaturated aliphatic hydrocarbons in a sulphuric acid vehicle or more broadly in halogenating under such conditions. Whether or not the unsaturated material forms a definite compound with the sulphuric acid or merely a solution, is not an essential consideration herein, the product obtained with sulphuric acid being treated with chlorine or other halogen, or compound thereof, to yield suitable halogenated products, which may be separated from the sulphuric acid and purified as halogen derivatives of said unsaturated material.

What we claim is:—

1. The process of making chlorinated hydrocarbons or other chlorinated bodies which comprises subjecting acid extract to the action of chlorine gas.

2. The process of making chlorinated hydrocarbons or other chlorinated bodies which comprises subjecting acid extract to the action of a chlorinating agent.

3. The process of making halogenated hydrocarbons or other halogenated bodies which comprises subjecting acid extract to the action of a halogenated agent.

4. The process of making halogenated products from the unsaturated hydrocarbons of gasoline which comprises extracting gasoline containing unsaturated bodies with an
65 extracting agent comprising sulphuric acid

of a strength corresponding to about 1.8 specific gravity whereby an acid extract is formed and in reacting on said acid extract with a halogen-introducing agent.

5. The process of making halogenated products from the unsaturated hydrocarbons of gasoline which comprises extracting gasoline containing unsaturated bodies with an extracting agent comprising sulphuric acid whereby an acid extract is formed and in
75 reacting on said acid extract with a halogen-introducing agent.

6. The process of making chlorinated products from the unsaturated hydrocarbons of gasoline which comprises extracting gasoline containing unsaturated bodies with an extracting agent comprising sulphuric acid of a strength corresponding to about 1.8 specific gravity, whereby an acid extract is formed and in reacting on said acid extract
85 with chlorine.

7. The process of making chlorinated products from the unsaturated hydrocarbons of gasoline which comprises extracting gasoline containing unsaturated bodies with an extracting agent comprising sulphuric acid whereby an acid extract is formed and in reacting on said extract with chlorine.

8. The process of making halogenated products from the unsaturated hydrocarbons of gasoline which comprises treating gasoline containing olefin material with sulphuric acid of a strength corresponding to about 1.8 specific gravity, whereby an acid solution is formed and in reacting on said
100 acid solution with a halogen-introducing agent.

9. The process of making halogenated products from olefine hydrocarbons which comprises extracting liquids containing olefine hydrocarbons with sulfuric acid whereby a reactive acid extract is formed, and in reacting on said acid extract with a halogen-introducing agent.

10. The process of making chlorinated hydrocarbons which comprises exposing acid extract to chlorine gas and withdrawing the heat of reaction.

11. The process of making chlorinated bodies which comprises exposing diluted acid extract of an acid strength corresponding to about 1.7 specific gravity to the action of chlorine.

12. The process of making chlorinated derivatives of hydrocarbons, which comprises adding water to acid extract and exposing it to the action of a chlorinating agent.

13. The process of making halogenated derivatives of hydrocarbons, which comprises adding water to acid extract and exposing it to the action of a halogenating agent.

14. As a new article of manufacture, a mixture of chlorinated hydrocarbons substantially from saturated hydrocarbons and
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derived from olefines of cracked petroleum by sulfation of said olefines to form a reactive acid extract followed by chlorination of the acid extract.

- 5 15. As a new article of manufacture, a mixture of halogenated hydrocarbons, substantially free from saturated hydrocarbons derived from olefines of cracked petroleum by sulfation of said olefines to form a re-
- 10 active acid extract, separation of the reactive acid extract from saturated hydrocarbons, and halogenation of the said extract.
16. The process of halogenation which

comprises dissolving an olefin in sulphuric acid and combining halogen therewith. 15

17. The process which comprises chlorinating an olefin in sulphuric acid.

18. The process which comprises chlorinating an olefin concentrate in an acid comprising sulphuric acid. 20

19. The process which comprises chlorinating unsaturated aliphatic hydrocarbons principally of the olefine type in a sulphuric acid vehicle.

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