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PROCESS OF MANUFACTURING IRON TETRACARBONYL

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This invention relates to a process of manufacturing iron tetracarbonyl, $Fe(CO)_4$. More particularly this invention relates to a simple and efficient process of producing iron tetracarbonyl directly from iron pentacarbonyl.

Heretofore in the manufacture of iron tetracarbonyl it has been necessary first to prepare iron nonacarbonyl or iron enneacarbonyl from iron pentacarbonyl and then prepare the iron tetracarbonyl from the enneacarbonyl. In accordance with this invention, however, the preparation of the iron nona- or ennea-carbonyl is eliminated.

Iron pentacarbonyl, $Fe(CO)_5$, may be formed by contacting carbon monoxide with finely divided metallic iron at elevated temperatures and pressures. The pentacarbonyl may be removed from the reaction vessel as a gas or vapor and then may be subsequently condensed to a liquid in which form it exists at atmospheric temperatures and pressures.

During the preparation of iron pentacarbonyl, temperatures of from about 350° F. to 400° F. may be employed. The iron pentacarbonyl thus produced is unstable in the presence of light, decomposing to yield a compound known as iron enneacarbonyl, $Fe_2(CO)_9$, which is precipitated as an orange-red insoluble solid. Carbon monoxide is evolved in the decomposition and such decomposition is rapid in bright light but slowly reversible in the dark, with the reformation of the pentacarbonyl.

Iron tetracarbonyl, $Fe(CO)_4$, may be formed from the enneacarbonyl by heating the enneacarbonyl in the presence of ether, toluene, triethylamine or light petroleum oils to temperatures not exceeding about 212° F. A bright green solution is formed when toluene is employed for example, and upon cooling the mixture under proper conditions, green crystals of the tetracarbonyl may be obtained. These iron carbonyls, and particularly iron tetracarbonyl, can be advantageously employed in motor fuels for permitting said fuels to operate at increased compression ratios in internal combustion engines.

An object of this invention is to disclose and provide a process of manufacturing iron tetracarbonyl directly from the pentacarbonyl without the necessity of forming the enneacarbonyl as an intermediate.

Another object is to disclose and provide a simple and rapid method of manufacturing iron tetracarbonyl.

A still further object is to disclose and provide manufacturing conditions under which iron tetracarbonyl may be produced directly from iron pentacarbonyl.

These and other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description of the preferred mode of operation and all modifications thereof.

It is to be understood that the invention is not limited to the precise steps employed nor to the use of the specific materials particularly stated herein, as those skilled in the art will readily understand the various modifications and substitutions of material which can be employed in adapting this invention to the manufacture of other metallic carbonyls under various operating conditions.

In carrying out the invention, iron pentacarbonyl in liquid form or in gaseous form, or a solution of iron pentacarbonyl in a suitable organic solvent such as benzene, ether or gasoline, is mixed with an alkaline solution and the agitation is continued until the pentacarbonyl is completely or substantially completely dissolved in the alkaline solution.

When pentacarbonyl in gaseous form is employed, it may be repeatedly passed through an alkaline solution until the desired quantity of the pentacarbonyl is dissolved in such alkaline solution.

A solution of pentacarbonyl in an aqueous liquid is evidenced by the deepening in color of the alkaline solution to an amber shade and by the lightening in color of the organic solvent if a solution of the pentacarbonyl was originally used. A solution of the pentacarbonyl may also be evidenced by the disappearance of the immiscible layer of pentacarbonyl when no organic solvent was originally employed.

The alkaline solution in which the pentacarbonyl is dissolved may be aqueous or alcoholic. The alkaline solutions used should preferably be five per cent or more in strength as the extraction of the pentacarbonyl is slower in more dilute solutions and larger amounts of liquid must therefore be handled to no advantage in the process. Instead of aqueous alkaline solutions, however, alcoholic alkaline solutions may be used for the extraction, the rate of solution for the pentacarbonyl in alcoholic solutions being highter than in aqueous alkaline solutions, due to the solubility of iron pentacarbonyl in alcohol.

The alkali used in the alkaline solution is preferably a strong alkali, such as sodium or po-

tassium. Weaker bases, such as ammonium hydroxide, may also be employed but the rate at which the pentacarbonyl is dissolved in such weaker bases is much lower than when strong alkalis are used.

The mixture of iron pentacarbonyl and of alkaline solution may have to be agitated for an appreciable period of time. Agitation for an hour or more may be required, depending upon the type of rapidity or agitation used, as well as the character of the alkaline solution employed. The extraction may be carried out at atmospheric temperature and pressure, although the use of higher temperatures increases the rate of solution of the pentacarbonyl in the alkali. When higher temperatures are employed, however, pressures above atmospheric are desirable so as to prevent loss of the pentacarbonyl (and of the organic solvent, if present) by evaporation and to prevent decomposition of the pentacarbonyl.

When a large amount of iron pentacarbonyl is dissolved in an aqueous caustic solution and the solution is allowed to stand for several hours, orange colored crystals will separate out. When dry, these crystals take fire spontaneously on exposure to the air, leaving ferric oxide. High concentrations of iron pentacarbonyl in the caustic solutions should therefore be avoided, or if high concentrations are produced, precaution should be taken against the accidental separation and drying of these crystals.

The alkaline solution of the pentacarbonyl made as described hereinabove, is now acidified by the addition of an acid and preferably a strong acid, such as hydrochloric or sulfuric acid. A gas, probably carbon monoxide, is evolved upon the acidification of the alkaline solution of iron carbonyl, and iron tetracarbonyl is precipitated as an amorphous green solid.

The reaction is completed when the amber color of the pentacarbonyl solution disappears entirely. When strong acids, such as hydrochloric or sulfuric, are used for the precipitation of iron tetracarbonyl, it may be desirable to cool the solution during acidification so as to prevent an appreciable rise in temperature.

The iron tetracarbonyl so produced may then be separated from the liquid by any convenient means, such as filtration, centrifugal separation or settling. Instead of employing these modes of separating the tetracarbonyl from the solution, the tetracarbonyl may be extracted by means of an organic solvent, such as benzene, toluene or light petroleum oils such as gasoline. If it is intended that the tetracarbonyl be employed subsequently in solution, then the extraction of the tetracarbonyl by means of a solvent is an obviously convenient procedure.

The tetracarbonyl produced in accordance with the method described hereinabove, is practically chemically pure, and it is not necessary to purify it further for all ordinary purposes.

Weak acids, such as acetic or butyric, are preferably not employed in acidifying the alkaline pentacarbonyl solution as upon the addition of weak acids, the iron tetracarbonyl will not be formed as an insoluble precipitate which can be readily removed from the solution by chemical means. The gas above referred to, probably carbon monoxide, is evolved, however.

When weak acids are used, instead of the formation of tetracarbonyl as an insoluble precipitate, a deep red solution results and iron tetracarbonyl may be extracted from this deep red solution with gasoline, benzene or other suitable solvent. It is preferred to carry out the acidification with a stronger acid, however, and to precipitate the tetracarbonyl as a solid.

In actual practice, the process has been conveniently carried out as follows: Nine parts of iron pentacarbonyl, either as the compound itself or in solution in an organic solvent, are dissolved in ten per cent sodium hydroxide solution containing four parts NaOH. This solution is acidified with twenty-five per cent sulfuric or hydrochloric acid which is added slowly to the solution with accompanying cooling. The precipitated iron tetracarbonyl is then removed from the solution in any desired manner.

It will thus be seen that the entire process is a simple one and easily carried out, without the necessity of highly skilled chemical control. Alkalis of a great range of concentration may be used in dissolving the pentacarbonyl; acids of a great range of concentration may be used in the acidification and precipitation of the tetracarbonyl. The process is characterized by the fact that the enneacarbonyl need not be formed at all. Moreover, a product of greater purity is produced, as, by the existing processes some pentacarbonyl contaminates the tetracarbonyl ordinarily produced.

All such changes and modifications as come within the scope of the appended claims are therefore embraced thereby.

I claim:

1. In a process of manufacturing iron tetracarbonyl, the steps of forming a solution of iron pentacarbonyl in an alkaline liquid, and then acidifying the alkaline solution with a mineral acid.

2. A process of manufacturing iron tetracarbonyl, comprising forming a solution of pentacarbonyl in an alkaline liquid, acidifying the solution thus formed by the addition of a strong acid, and separating iron tetracarbonyl from the acidified solution.

3. A process of manufacturing iron tetracarbonyl, comprising forming a solution of pentacarbonyl in an alkaline liquid, agitating the mixture, acidifying the alkaline solution by the addition of a mineral acid, and then separating iron tetracarbonyl from the acidified solution.

4. A process of manufacturing iron tetracarbonyl, comprising dissolving iron pentacarbonyl in an alkaline solution with agitation, acidifying the resulting solution with a mineral acid, and extracting iron tetracarbonyl from the acidified solution with an organic solvent.

5. A process of manufacturing iron tetracarbonyl, comprising dissolving iron pentacarbonyl in an alkaline solution with agitation at a pressure sufficient to prevent decomposition of iron pentacarbonyl, acidifying the alkaline solution with a mineral acid, and then separating iron tetracarbonyl from the acidified solution.

6. A process of manufacturing iron tetracarbonyl, comprising dissolving iron pentacarbonyl in an alkaline solution, acidifying the mixture with mineral acid to precipitate iron tetracarbonyl, and then separating iron tetracarbonyl from the acidified solution.

7. A process of manufacturing iron tetracarbonyl, comprising agitating a solution of iron pentacarbonyl in an organic solvent with a solution of a strong base, acidifying the resulting alkaline solution with strong acid, and extracting the acidified solution with an organic solvent for iron tetracarbonyl.

8. A process of manufacturing iron tetracarbonyl, comprising forming a solution of iron pentacarbonyl in an alcoholic alkaline liquid, acidifying the mixture thus formed with strong acid, and then separating iron tetracarbonyl from such acidified solution.

9. A process of manufacturing iron tetracarbonyl, comprising dissolving iron pentacarbonyl in an alkaline solution, acidifying the alkaline solution thus formed with a mineral acid, cooling the acidified mixture, and separating iron tetracarbonyl from the acidified solution.

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