The energy costs of electrolytic reduction compared to costs of chemical reducing agents appear to show a fair margin in favor of the former except for the very cheapest reducing materials, such as iron (7). An opportunity for reducing the cost of electrical energy is in the use of off-peak power.

With all the research that has been carried out in this field, the possibilities of the electrolytic method of reducing organic compounds are still undetermined, and more fundamental work is needed to overcome the uncertainties that exist.

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# Esterification

# Manufacture of Malonic Ester

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A brief outline is given of the chemistry of malonic ester (diethyl malonate) manufacture, emphasizing the quantitative application of the unit process, esterification. to industrial production. The

THE classical malonic ester synthesis has, in recent years, received more than its share of consideration in the process industries. This has been due to the popularity of the barbiturates, a class of compounds for which malonic ester (diethyl malonate) is generally considered the starting material. The preparation of this chemical in the laboratory is a procedure well known to all organic chemists. Its manufacture on an industrial scale, however, presents many problems unknown to the laboratory technician, and this phase of the subject is to be discussed here.

The chemistry of this esterification process is generally so well known that it will be mentioned only briefly. The process depends upon the following reactions:

$$\begin{array}{ccc} Cl & Cl \\ CH_2COOH + NaOH \longrightarrow CH_2COONa + H_2O \\ Cl & CN \\ CH_2COONa + NaCN \longrightarrow CH_2COONa + NaCl \\ CN \\ 2CH_2COONa + 4C_2H_5OH + 5H_2SO_4 \longrightarrow \\ COOC_2H_5 \\ 2CH_2 & + Na_2SO_4 + 2NH_3 + 4SO_5 + 4H_2O \\ COOC_2H_5 \\ 2COOC_3H_5 \end{array}$$

In the plant these reactions are accomplished in the following steps: (1) neutralization of the monochloroacetic acid with

chemical engineering principles involved in the straight-line production of this reagent are described; type and design of equipment, flow and transfer of materials, etc., are given.

sodium hydroxide, (2) reaction of the formed sodium monochloroacetate with sodium cyanide, (3) concentration of the resulting mixture to a "cake," (4) hydrolysis of the cake by sulfuric acid and subsequent esterification of the "nascent" malonic acid by ethyl alcohol, (5) extraction of the malonic ester with benzene, (6) purification of the benzene extract, and (7) removal of the benzene by distillation.

Through various improvements in the method of manufacture over a period of years, this material is now produced in the plant by this process with an average yield of 70 per cent. When assayed by means of the saponification value, it contains not less than 90.0 per cent malonic ester, and the acidity in terms of malonic acid is less than 0.1 gram per 100 The material thus obtained is not a colorless liquid as cc. described in the literature but has a slight yellow or straw color. It can be rendered colorless by fractionation, but since it is used in malonic ester syntheses, it seems economically inadvisable to purify the material further.

A few years ago it became desirable to segregate this process from the manufacture of other chemicals because of the hazardous nature of one of the reagents used-namely, benzene. After careful study, therefore, the process was installed in an isolated building as a distinct unit process, where production was accomplished on a straight-line basis. The flow sheet evolved is shown in Figure 1.

#### Housing for the Process

This structure, made of red-faced reinforced brick, is 30 feet long, 18 feet wide, and 28 feet high, inside dimensions.

# INDUSTRIAL AND ENGINEERING CHEMISTRY



SODIUM CYANOACETATE ("CAKE") STILL

Above and in the center of the roof is a Transite monitor, 12 feet long, 10 feet wide, and 7 feet high, in which is housed the exhaust fan for the ventilating system of the building and a three-stage Elliott steam ejector-condenser. The floor and ceiling of the building are concrete; the interior walls are white glazed brick. There are eight windows, three on each side and one on each end; each one practically fills an entire bay, except in the two bays where the doors are located. All of the sashes of these windows are operable so that there is good natural ventilation. Besides the ground floor, there are two mezzanines or working platforms at the 5- and 18-foot levels. Located just outside of the building is the storage space for the chemicals used in this process, such as sodium cyanide, monochloroacetic acid, sulfuric acid, etc.

## **Engineering Details**

The manufacture of the ester begins in a 300-gallon stoneware jar located on the ground floor, in which are placed the

monochloroacetic acid and an equal weight of ice. The acid is neutralized with a 50 per cent solution of sodium hydroxide which is run into the jar from a 300-gallon iron storage tank located on the upper mezzanine, where a week's supply has been previously prepared. The heat of neutralization of this reaction melts the ice, thereby yielding a cool solution of sodium monochloroacetate. Agitation of the acid and ice during this neutralization is accomplished by a Lightnin mixer.

This solution of sodium monochloroacetate is next drawn by vacuum into a 900-gallon jacketed iron still on the upper mezzanine where it is warmed to  $60^{\circ}$  C. (140° F.) with steam. After adjusting the pH of the solution to about 9.0, a hot concentrated solution of sodium cyanide is added. This cyanide solution has been previously prepared in an adjacent 150gallon jacketed iron tank and is allowed to run slowly into the warmed solution of sodium monochloroacetate, resulting in a vigorous reaction, accompanied by a great amount of foaming and a rapid evolution of cyanide vapors which have to be exhausted from the still by an efficient ventilating fan.

When this reaction is complete, the mixture is concentrated under the vacuum of the jet condenser to about one-fourth of its original volume. This "cake," as it is termed in the plant, is a thick semisolid mass which flows readily when hot but immediately solidifies upon cooling. It is dumped through the bottom outlet by means of an iron chute into one of two 500-gallon Pfaudler glasslined reaction kettles located on the lower mezzanine. This kettle contains warm, specially denatured alcohol which, incidentally, has been recovered from other malonic ester syntheses and is at least 99.5 per cent pure.

This esterification is a batch process which runs for about 36 hours. Thus, starting a new batch every morning, today's lot will have been processed up to the above point while yesterday's lot is being extracted from the reaction mixture. This is accomplished by using two reaction kettles; each one is charged on alternate days from one cake still.

The reaction kettles are equipped with anchor-type directdriven agitators and 9-foot vertical brass reflux condensers, the vapor pipes of which lead into scrubbing towers where the evolved gases of the reaction are washed down the sewer with showering sprays of water. The kettles are also connected to a pipe line leading to a 185-gallon iron sulfuric acid charger. This latter is filled with a definite weight of commercial sulfuric acid from the glass carboys under 12 to 15 pounds per square inch of air pressure.

After the reaction kettle has been charged with the alcohol, which is pumped from 50-gallon drums, and with the cake, the acid is blown into the kettle from the acid charger under air pressure controlled by a Taylor temperature regulator. In this way the rate of addition of the acid is automatically controlled and depends upon the temperature and rate of reaction of the mixture within the kettle. When all the acid has been added, the entire mixture is gently refluxed overnight by heating with steam.





MALONIC ESTER REACTION STILLS

The following morning there is added to the still an amount of distilled water equivalent to about one-fourth of the reaction mixture and an equal quantity of benzene, pumped from a 1000-gallon underground storage tank. This entire mixture is agitated and mixed intimately, and then allowed to settle and separate. The benzene, extracting out the malonic ester, rises as a top layer and is pumped off by a Duriron centrifugal pump into an adjacent 500-gallon Pfaudler glass-lined extraction tank, equipped with an anchor-type direct-driven agitator. Two additional extractions of the reaction mixture are made with benzene and added to the original extract in the extraction tank. Finally, three similar extractions of the reaction mixture are made with more benzene. However, these extracts are pumped by the Duriron pump into a 300-gallon stainless steel storage tank located on the upper mezzanine, where they are held until the next day to be used as the first three extractions for the next batch of ester and are returned at that time to the reaction kettle by gravity. The reaction mixture is then washed from the still directly down the sewer.

The combined benzene extracts in the extraction tank are now washed twice by agitation with small amounts of distilled water, which are removed as a lower layer and discarded. The extracts are then washed twice by agitation with cold portions of 12.5 per cent sodium hydroxide solution, which are likewise removed as a lower layer and discarded. After one more washing with distilled water, the extracts are finally dried with dry sodium sulfate.

The dry benzene extracts of malonic ester are now pumped out of the extraction tank by a Blackmer rotary pump into a near-by 300-gallon Pfaudler glass-lined jacketed recovery still, leaving as a residue in the bottom of the extraction tank the sodium sulfate and a small portion of the benzene extracts. Both are removed through the bottom outlet and filtered on a gravity filter. The extract thus recovered is added as tailings to the next batch when the benzene extracts are removed from the reaction still and transferred to the extraction tank.

The extract in the recovery still is next subjected to distillation under atmospheric conditions until 75 to 80 per cent of the benzene has been recovered by the aid of a condenser in an iron receiver. After the still has been cooled somewhat by circulating cold water through its jacket, a 15-20 inch vacuum, supplied by the jet condenser, is applied to the apparatus and the remainder of the benzene is distilled off into the receiver. This benzene distillate is then returned to the 1000-gallon underground storage tank to be re-used in future batches.

The residue remaining in the recovery still is malonic ester which is not less than 90 per cent pure. It is run out of the bottom of the still through a Y-pipe containing a strainer made of No. 20 mesh screen wire. This strainer, which can be readily emptied after each batch, serves as a filter to remove any last traces of sodium sulfate that may have been accidentally pumped into the recovery still from the extraction tank along with the benzene extracts. After passing through the strainer, the malonic ester is transferred by the Blackmer rotary pump to individual iron storage tanks, located on the upper mezzanine. These tanks are equipped with calibrated gage glasses so that the yield and percentage of yield of each batch can be easily determined.

These tanks are connected by individual bottom outlets and valves to a common header pipe which transfers the ester by gravity to the proper location in a neighboring building where it is used in subsequent malonic ester syntheses.

This paper discusses only the present working conditions of this esterification process. Naturally many problems had to be solved and much experimentation on a large scale had to be done before discovering the correct equipment, the right layout, and the proper manufacturing procedure to give the optimum results.

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