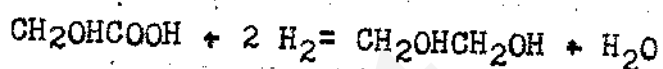
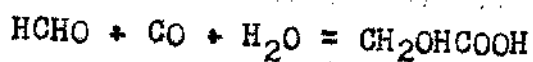

PART I

INTRODUCTION

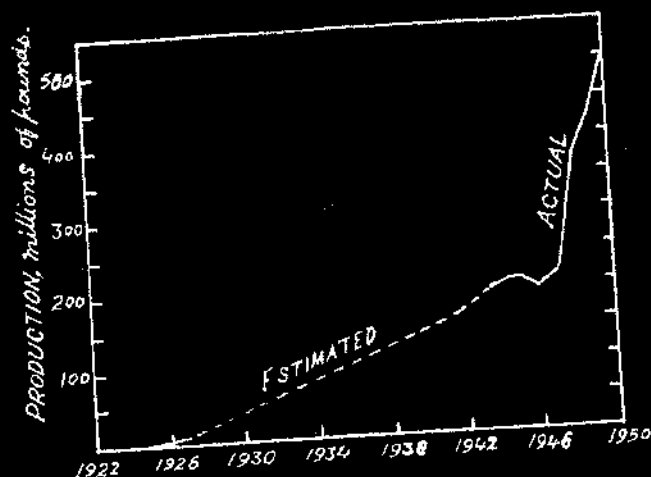
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INTRODUCTION

Glycollic acid (alpha-hydroxyacetic acid, CH_2OHCOOH) is an organic chemical of great industrial importance, primarily because it is an intermediate in the two-stage synthesis of ethylene glycol from formaldehyde:



Glycollic acid has, in addition, a number of other uses and its derivatives are employed in a number of industries, especially as high boiling solvents, as plasticisers and softening agents for cellulose esters and ethers, natural and synthetic resins, etc., in liquid coatings, brake-fluids, antiseptics and insecticides, as insolubilisers for polyvinyl alcohol plastics, as adhesives, coating compositions and impregnants for paper, as additives to highly refined lubricating oils, as sticking substitutes for gums, for dye-coating of aluminium alloys, in baths for bright dip for copper and alloys, and in colour and stain removers for fabrics. Glycollic acid is also used as a peptizing agent for electromagnetic hydrosols, for aerial disinfection of air, and in coagulation of rubber in which it is 15 - 20% better than formaldehyde. Titanium derivatives of glycollic acid find uses as modifiers for synthetic resins. In



USE PATTERN

	per cent
ANTIFREEZE	65
DYNAMITE	5
GELLOPHANE	5
MISCELLANEOUS AND EXPORT	25
	<hr/> 100

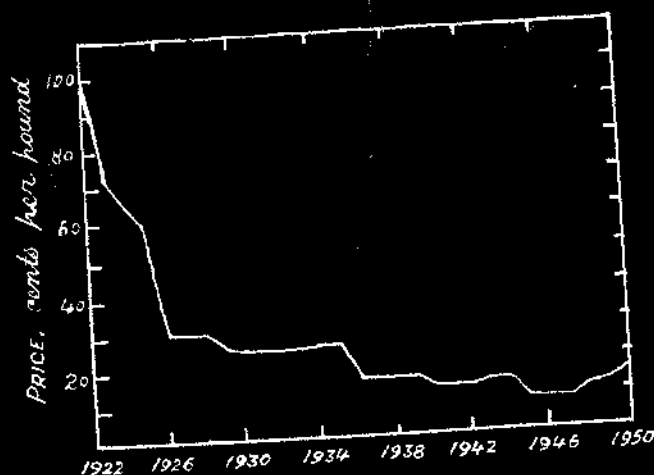


FIG.1 ETHYLENE GLYCOL.— PRODUCTION, PRICE AND USE
IN THE U.S.A

experimental chemistry, glycollic acid and its derivatives are employed as intermediates in organic synthesis as, for example, for the hydroxy-acetylation of 9,11-diricinolein dimer to yield a product of extensive industrial importance, as catalysts for the cleavage of CO from formamide and, as sodium starch glycollate, in oxidation-reduction indicators and in iodometric analysis, especially for microdetermination of iron. Urotropic salts of glycollic acid are in use as solvents for uric acid and as antiseptics of the urethra.

There are no direct economic data available on the production and consumption of glycollic acid, since most of the manufacturers are themselves the principal users. Data are, however, available on the overall production of ethylene glycol in the United States of America; fig. 1 shows production, price and use statistics based on U.S. Tariff Commission reports and other sources⁶⁷. Since the manufacture of ethylene glycol from glycollic acid is one of the economically competitive processes, the consumption of glycollic acid may be expected to show a corresponding rise with the rapidly increasing world production of ethylene glycol. Thus, in the eleven years preceding 1951, the production of glycollic acid by the high pressure process utilising acidic catalysts increased 180 per cent at the Belle plant of E.I. du Pont de Nemours

& Co., Inc., the originators of the process⁶⁸.

Numerous processes have been patented for the preparation and the manufacture of glycollic acid from various raw materials. Technically, the usual method of obtaining glycollic acid is the electrolytic reduction of oxalic acid^{69,70}, dissolved in dilute sulphuric acid, using lead electrodes:



Other methods include the oxidation of ethylene in the presence of sodium hydroxide with a high counter-current velocity to produce glyoxal and glycollic acid⁷¹; reduction of a monoalkyl ester of oxalic acid at 100 - 150 atmospheres in presence of nickel or some other catalyst to produce glycollic acid or its salts⁷²; catalytic hydrogenation of oxalic acid itself to yield glycollic acid⁷³⁻⁷⁶; preparation by heating together cupric acetate and the solution of an acetate of an alkaline earth metal to 160 - 200°C. under pressure⁷⁷; hydrolysis of chloroacetic acid under pressure⁷⁸⁻⁸⁰; interaction of formaldehyde and methyl formate to produce propyl glycollate⁸¹; hydroxymethyl cyanide hydrolysis to glycollic acid⁸²; and the preparation of sodium glycollate by the action of sodium hydroxide on aqueous polyglyoxal hydrate⁸³. Such methods as glycine-nitrous acid reaction to yield glycollic

acid, nitrogen and water⁸⁴, interaction of ammonium chloride and sodium carbonyl in presence of liquid ammonia⁸⁵, or mild oxidation of ethylene glycol with nitric acid are⁸⁶, as may be expected, only of an academic interest.

The high pressure process for the manufacture of glycollic acid from formaldehyde, carbon monoxide and water presents the possibilities of some variations of considerable technical and theoretical importance. Replacement of water by methyl alcohol, ethyl alcohol or some other monohydroxy alcohol leads to the formation of the corresponding ester of glycollic acid^{65,66}. Likewise, polyhydric alcohols and their derivatives, e.g., ethylene glycol as well as its monomethyl, monoethyl and other ethers, may be employed. Inorganic substituted acetic acids are produced when an inorganic acid, like hydrochloric acid, is used in place of water⁶⁴. By this method, chloroacetic, bromoacetic, fluoroacetic, phosphoroacetic, mercaptoacetic acids and sulphuric, sulphurous and boric esters of hydroxyacetic acids may be produced. Use of polybasic acids causes one or more of their hydrogen atoms to be replaced by one or more oxyacetic groups respectively. If organic acids are used for the reaction in place of water, esters of the hydroxy group in glycollic acid with the respective organic acid are formed. Instead of formaldehyde, acetaldehyde or

GLYCOLLIC ACID

GLYCOLLIC ACID

MIXING TANK

WATER

SULPHURIC ACID

SCRUBBER

FORMALDEHYDE AND WATER VAPOURS

REACTOR

CARBON MONOXIDE

VACUUM STILL

GLYCOLLIC ACID

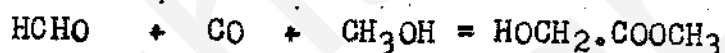
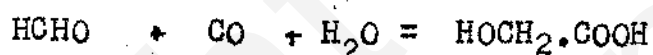
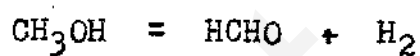
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or some other aldehyde may be used, thus yielding lactic or higher hydroxy-acetic acids.

The industrial high pressure process⁸⁷ for the manufacture of glycollic acid, uniquely operated by du Pont at Belle, West Virginia, U.S.A., although never fully described in literature, is believed to involve interaction of formaldehyde, carbon monoxide and water at some unspecified pressures and temperatures in the range of 5 to 1500 atmospheres or more and between 125° and 225°C. In the continuous process⁶⁷, vapours consisting of one part formaldehyde and one part water, such as are obtained by the catalytic oxidation of methanol, are said to be passed into the bottom of a scrubbing column. Here they contact a solvent mixture, containing, on a molal basis, two parts of glycollic acid, one part of water and approximately 0.02 parts of sulphuric acid. The resulting solution leaving the bottom of the column (2 parts glycollic acid, 1 part formaldehyde, 2 parts water, and 0.02 part sulphuric acid) is passed through a continuous reactor in the presence of carbon monoxide in excess. It is believed that the pressure employed is of the order of 700 atmospheres at 200°C. The resultant mixture produced is distilled under 80 to 100 mm. Hg pressure at such conditions that glycollic acid is removed from the bottom of the column; the overhead vapours (2 parts glycollic acid

and 1 part water) are returned to the scrubber to absorb more formaldehyde and water. The process is illustrated in the flow-sheet shown in fig.2.

The glycollic acid thus obtained may be esterified with an alcohol^{88,89} such as methanol, and then hydrogenated to ethylene glycol⁹⁰⁻⁹⁵ :



A number of patents⁹⁶⁻¹⁰⁰ cover the purification of glycollic acid and its crystallisation from the product obtained by this high pressure and other technical reactions.

Carbon monoxide and formaldehyde are the two raw materials employed for the synthesis of glycollic acid by the high pressure process. Though no precise data are available on the world production of carbon monoxide, its potential availability as a cheap raw material for chemical synthesis is indeed enormous. The largest source of carbon monoxide used for the various industrial processes is to be found in the gases made from coal and coke by blue water generators, producers, blast furnaces, and coke ovens. The carbon monoxide

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content in the gases produced by these methods is, by volume, 37.8 - 42.8%, 22.0 - 26.0%, 26.2 - 27.5% and 5.0 - 6.8%, respectively¹⁰¹. Blue water gas contains the highest percentage of carbon monoxide and is most frequently employed as a source of pure carbon monoxide. Even higher proportions of carbon monoxide may be produced by blowing a water gas set with carbon dioxide, instead of steam, over hot coke. In areas producing natural gas and petroleum, carbon monoxide may be produced by reacting the hydrocarbon gases with oxygen, air, steam, or carbon dioxide. Various by-product gases also contain carbon monoxide in insufficient concentration for use on a limited scale.

The theoretical daily consumption of carbon monoxide gas in the United States in 1947 for the manufacture of synthetic methanol alone was estimated to be as high as 17.3 million cubic feet¹⁰².

Formaldehyde is a product of an outstanding commercial value. It has extensive uses in the field of synthetic resins, chemical synthesis, textile and paper industries, agriculture, disinfection and embalming, leather and fur industries, chemicals and pharmaceuticals, photography, etc. The properties which make formaldehyde of value are due principally to the high order of ^{its} chemical reactivity, its

colourless nature, its stability and the purity of its commercial forms. The utility of formaldehyde from the use viewpoint is manifested as a resinifying agent, tanning agent, stiffening agent, disinfectant, bactericide and preservative. During the process of chemical synthesis, formaldehyde acts in such a manner that similar or dissimilar molecules and radicals get fastened together by means of methylene linkages¹⁰³.

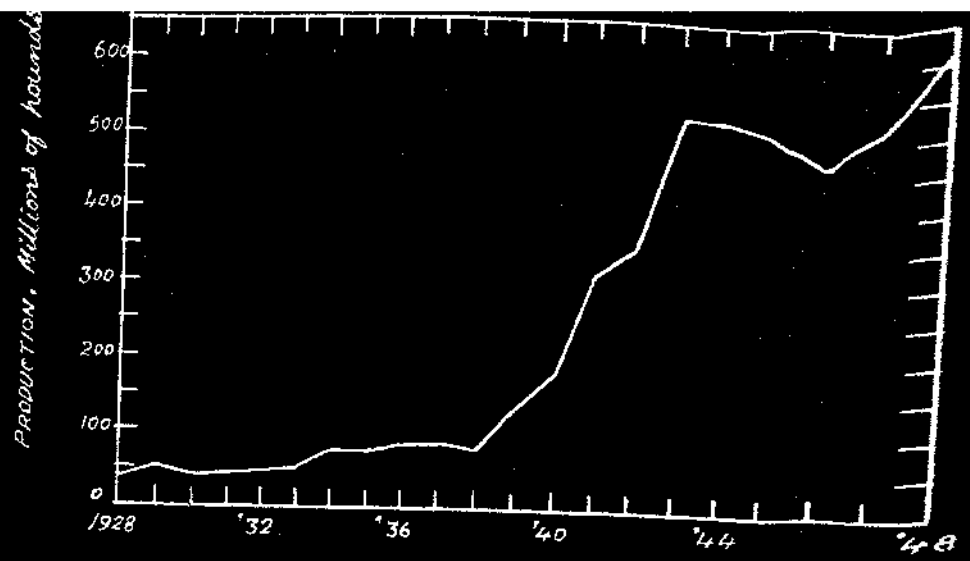
Commercially, formaldehyde is available chiefly in the form of an aqueous solution containing 37 - 41% HCHO by weight dissolved along with methanol upto 15%. The latter is present in an amount sufficient to prevent precipitation of the formaldehyde polymers under ordinary conditions of transportation and storage. Other forms in which formaldehyde is marketed to a somewhat lesser extent are: solutions containing less than 1% methanol; paraformaldehyde; trioxane; and hexamethylene tetramine, formed by the interaction of formaldehyde and ammonia and substituting the former for a number of important industrial reactions. Formaldehyde is manufactured mainly through air oxidation of methanol¹⁰⁴⁻¹⁰⁹ and through oxidation of paraffin hydrocarbons¹¹⁰⁻¹¹². In the latter case, methane may be the starting material, or a higher hydrocarbon,^{113,114} such as ethane, propane or butane, may be oxidised to yield several products of which formaldehyde may be one.

The large availability of formaldehyde for the

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The large availability of formaldehyde for the



USE PATTERN

	per cent:
RESINS	60
HEXAMETHYLENETETRAMINE	4
PENTAERYTHRITOL	12
ETHYLENE GLYCOL	4
OTHER CHEMICALS	12
MISCELLANEOUS	8
	100

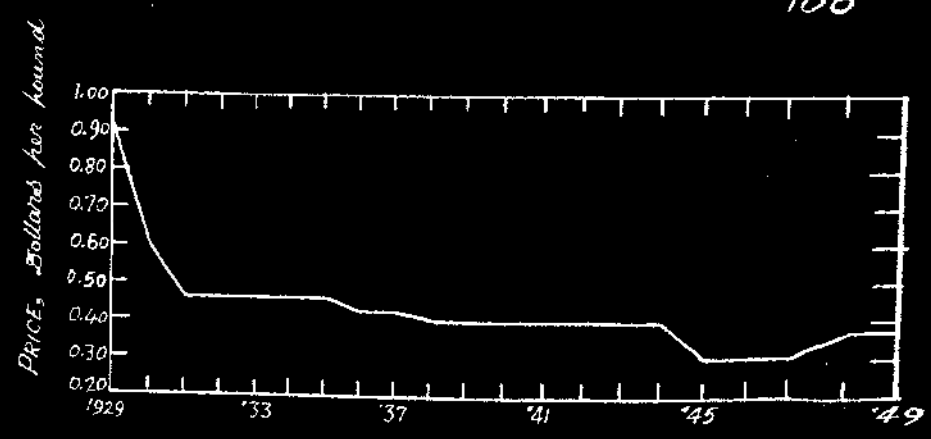


FIG. 2a. FORMALDEHYDE (37%), - PRODUCTION, PRICE AND USE PATTERN IN THE U.S.A

purpose of chemical syntheses and other uses may be gauged by the very large production figures⁶⁷ for this important raw material of industry, shown, along with price and use statistics, in fig.3.

A number of catalysts, especially of an acidic character as stated earlier, have been employed for the synthesis of carboxylic acids from carbon monoxide. As is well known, nickel^{115,116} and other elements of the I transition group and their salts have in recent years been increasingly employed in organic synthesis. The use of halide catalysts, particularly of nickel, has been reported for carboxylic acid synthesis by Reppe and Kutepow¹⁵, Carpenter¹⁸, and Woodhouse¹⁴. These catalysts have been subject of an intensive investigation by Bhattacharyya and his coworkers and have been employed by them for the syntheses of acetic³⁴⁻³⁷, propionic^{44,45}, formic¹⁷, adipic⁴⁷ and lactic⁵⁸ acids. In the present work, halides of nickel, cobalt and iron, particularly the iodides, have been used for the syntheses of glycollic acid from formaldehyde, carbon monoxide and water, of methyl glycollate from formaldehyde, carbon monoxide and methanol, and of ethyl glycollate from formaldehyde, carbon monoxide and ethanol. A study of the various reaction variables has indicated that these products can be obtained in high yields by the use of iodide catalysts.