Some Newer Aspects of Glycerine

By KENNETH HOOVER, Miner Laboratories, Chicago

The industrial importance of glycerol, or glycerine as the commercial product is ordinarily known, dates from the work of Nobel who, having recognized the technical importance of glyceryl nitrate as an explosive, discovered in 1868 that this compound, which had previously been regarded as a dangerous laboratory curiosity, could be rendered comparatively safe by absorption in kieselguhr. It is interesting to note that the use of glycerine which originally established its commercial importance has since remained the largest outlet for glycerine, and glyceryl nitrate or nitroglycerine as it is more commonly known, has since been a most important instrument in both peace and war. Explosives composed wholly or in part of nitroglycerine and closely related substances remain the most important of industrial explosives.

Ranking second only to the explosive field in volume of glycerine consumed has been the field of tobacco products. It is usually a matter of distinct surprise to those not previously informed to learn that this is not only the second largest use of glycerine but that the consumption in the United States has approximated 25 per cent of the total production of glycerine; but believe it or not, glycerine is necessary for the production of your favorite cigarette, notwithstanding "costlier tobaccos," "choice blends," "the toasting process," or "the humidor pack," though of the latter more will be said later.

We have recently had occasion to determine glycerine in the leading brands of cigarettes and in pipe and plug tobaccos. The glycerine content of cigarette tobaccos was found to range from 1 per cent to 2.7 per cent on the "as is" basis, though only one tobacco showed less than 2.3 per cent. Pipe tobacco contained somewhat more glycerine, having approximately 3.2 per cent. One sample of plug tobacco was found to contain 2.2 per cent glycerine. The volatile matter of these tobaccos upon drying 18 hours at 100° C. was approximately 12 per cent, 15 per cent, and 17 per cent for cigarette, pipe, and plug tobacco respectively, so that on a dry basis the quantities of glycerine used are considerably higher.

As previously stated, the application of glycerine which gave it prominence commercially has remained, even to the present, its largest use. Disregarding the period of the World War, when the production of explosives reached abnormal proportions and when glycerine was diverted, of necessity, from many of its normal applications, nitroglycerine production, even in the years following hostilities, consumed approximately fifty per cent of the glycerine production in this country; largely for industrial purposes. With the very substantial curtailment of constructional activities and industrial operations during the past few years of economic readjustment, there has been in consequence a sharp decrease in the consumption of glycerine for production of nitroglycerine. Notwithstanding this fact, glycerine production in the United States has not been reduced in great measure.

Glycerine is a by-product of soap manufacture, and its production is largely independent of consumer demands. Soap production during the past few years does not appear to have suffered seriously. Therefore, though the principal outlet for glycerine has greatly decreased in volume, glycerine production has continued almost unabated. During the past few years several writers have deplored the sad economic plight of glycerine, and one gathers that between the inroads made by substitute products and the threat of synthetic glycerine or its production by other than present means, the future of glycerine is not very promising to its producers. On the contrary it is the feeling of our group that glycerine is potentially in the soundest economic position it has ever been and for one reason alone—diversification of its consumption.

It does not appear likely that there are in the United States today any substantial stocks of glycerine. What then has taken up the slack of the important consuming channels? Glycerine is in fact finding new outlets, and research effort is contributing in large measure to the development of these new channels of consumption. The glycerine producers themselves are actively engaged in this research, and glycerine consumption in the future is less likely to be dependent upon the haphazard dictates of consumer demand.

One could not hope to include in this short paper all of the applications which have been proposed nor is there reason for doing so. Excellent articles describing its properties and uses have appeared during the past few years, and no attempt is made to review them here. Such articles have included, of course, a great many proposed uses which though of considerable interest from a technical viewpoint have never reached the stage of successful commercial exploitation. Likewise it is feared that some writers have attached too much importance to some of the uses merely suggested by patents or published accounts. For example, no review of the uses of glycerine seems to have been deemed complete without describing its application together with glue and water in the preparation of stable foams for use as a covering over gasoline in storage tanks to prevent evaporation losses. These foams in fact ultimately proved to be not so stable in actual service, and with the development of other means for the reduction of these evaporation losses, their use was abandoned. So far as we know, glycerine is not being used for this purpose today, and it is doubtful if more than a relatively small quantity ever was used. As a matter of fact had this application of glycerine proved successful, its potential consumption might have reached staggering proportions from the viewpoint of glycerine production.

The organization with which I am connected has been identified with the development of certain of the newer uses of glycerine and has naturally tried to follow the research activities in the field generally. A short survey of what appear, from a commercial point of view, to be

the most important new uses of glycerine may prove interesting to this group.

Perhaps the most interesting of the important new applications of glycerine is its use in the production of synthetic resins. A search of the patents in this field reveals the fact that glycerine enters into the manufacture of practically all classes of synthetic resins, but the "alkyd" or "Glyptal" resins which are made by esterifying polyhydric alcohols with polybasic acids have proved the most important of the resins involving the use of glycerine in their production. Although the first patents covering these resins were taken out approximately twenty years ago, it was not until the original patents had almost expired that practical applications of the resins were developed.

These resins first found important practical application as constituents of nitrocellulose lacquers where they were used to replace natural resins, and since that time their development for many applications has been both rapid and interesting. During the past few years considerable quantities of these alkyd resins have been produced annually for use as film forming materials, and their introduction has very materially changed the trend of the paint, varnish, and lacquer industry. Their present importance in the protective coating field has resulted largely because of the important combination of desirable properties which they possess generally. Important among these properties are exceptional weather resistance, ability to retain gloss over long periods, excellent flexibility, adhesion, and flow.

It has been estimated that some 9,000,000 pounds of these "Glyptal" resins were used last year in the manufacture of industrial finishes.

The adaptability of the alkyd resins to all sorts of techniques and conditions constitutes their chief significance. Many applications are still in the developmental stage, while others remain to be developed. It has been shown that these alkyd resins, by the adoption of suitable expedients, can be produced in soluble and insoluble forms, in both fusible and infusible states, and as soft, hard, flexible, or balsam-like resins. It has been demonstrated that these resins can, variously, be extruded in any size or shape in tube or ribbon form, they can be calendered in the manner of rubber or frictioned into cloth, they can be cast, or they can be molded as an ordinary thermoplastic, they can be made in any degree of flexibility, and they can be varied as to mechanical, electrical, and chemical properties.

When it is said that these alkyd resins offer a substitute for celluloid with the particularly important advantages of non-inflammability and further that the cured flexible resins can be compounded on rubber rolls and subsequently handled very much like rubber itself, we are already at the door of many important industrial applications.

In our own work we have developed interesting resins of this general type by utilizing instead of glycerine the aryl, alkaryl, and heterocyclic ethers of glycerine. By reaction with a polybasic acid such as phthalic acid or its anhydride, resins of the permanently fusible soluble type are produced which vary from soft balsam-like products to hard resinous bodies. They may be varied further by the use of modifying agents commonly known to the art.

The "humidor pack" previously referred to is one of the applications of transparent regenerated cellulose products which constitute one of the newer important outlets for glycerine. Unfortunately for present purposes, there is little that can be said about the use of glycerine in these products in view of the lack of published information regarding this application. However, during the past few years several million pounds of glycerine have been utilized annually by this industry, and the recent comparatively rapid development of these products has led to unique and interesting applications which are being extended constantly.

Of the newer outlets for glycerine which are being established, the most important in size at present is the anti-freeze field. It has been known for many years, of course, that glycerine in common with several of the alcohols was an efficient depressant of the freezing point of water, and its application to this use has not, therefore, resulted from any very recent discoveries concerning its physical properties. However, its development to meet the rigorous requirements of automotive usage has been the result of extensive research.

The first use of glycerine solutions as an automotive anti-freeze probably dates back fifteen or twent years. However, at that time we were generally more concerned with preparing our cars for winter storage than winter driving, and the volume of anti-freezing solutions required for the protection of automobiles certainly did not reach important proportions. Later when winter driving became the rule rather than the exception, the abnormal conditions previously referred to maintained the price of glycerine at a level where it was not economically feasible for anti-freeze use. As the effects of these abnormal conditions were dissipated, however, it became a possibility, particularly in view of certain inherent advantages which glycerine appeared to offer in contrast to the other available anti-freezing solutions. The glycerine producers themselves entered this field and pioneered the so-called "permanent" anti-freeze field.

Those connected with the radiator glycerine development were to learn soon that an ideal anti-freeze must do far more than depress the freezing point of water. Radiator glycerine was introduced in the anti-freeze field at the beginning of an era of unprecedented automotive engineering developments. The demands for reliability and comfort in automobiles having been satisfied in reasonable degree, there came demands for greater speed. Increased speed meant larger engines, multi-cylinder engines, higher compression of engines; in a word—greater power. Greater power meant larger amounts of heat to be dissipated and resulted in higher water pump speeds or pumps with greater volume displacement; in higher operating temperatures; and in increased radiating surface and, therefore, more and smaller radiator channels, because increase in frontal area has been limited by the trend of aerodynamic body design and styling, and increase in the depth of radiators is far less effective. These trends of engineering design imposed increasingly rigorous requirements upon anti-freezing solutions and coolants in general.

Extensive research on the part of the glycerine producers has been necessary to meet the problems of this automotive field. Its reward has been the establishment, in only a few years, of one of the most important of the newer outlets for glycerine, and continued research will maintain its dominant position in the "permanent" anti-freeze field. The volume of this outlet at present represents a very substantial percentage of the glycerine produced in this country. Its rapidly growing distribution by the producers themselves and more recently its very rapidly increasing distribution by the automobile manufacturers, presages an expansion of this outlet to almost any proportions desired by the producers.

The application of glycerine to food uses while not one of the newer applications is likely to become of increasing importance as a result of the physiological studies with glycerine conducted by A. J. Carlson, Victor

Johnson, and Adelaide Johnson of the University of Chicago, which were completed during the past year. These studies proved glycerine acceptable as food in the animal organism and without adverse subjective effects or physiological reactions in humans even upon the addition of as much as 110 grams glycerine per day to the diet. These careful studies seem to refute completely previously reported results of an adverse nature and a firm foundation seems to have been established on which to proceed with the application of glycerine to food uses.

Glycerine has been used in the past as a moistening, sweetening, and blending agent in food preparations and beverages. An increasing application of glycerine to bakery products is found at present, and it seems destined to find extended application in liquors and cordials, should the people of the United States abandon prohibition.

And now in closing just a word concerning a newer field, which, from a technical point of view is extremely interesting; and, one suspects, full of potentialities. That field broadly speaking is the field of glycerine derivatives. The literature evidences widespread investigation of a surprisingly large number of these derivatives. The esters of glycerine have, of course, received most attention and have found greater practical application at present. Other derivatives appear to be of even greater interest, both from a technical and practical viewpoint, and hold the promise of profitable return to those who investigate their development and commercial applications.

Important among these derivatives are the ethers, the amino derivatives, and the oxidation products of glycerine. Ethers of glycerine can be prepared having almost any desired boiling point ranging from 148° C. and up. Generally speaking they are colorless, stable compounds of mild odor and vary from mobile liquids to crystalline solids. They are characterized by excellent solvent powers which suggests their application to a wide range of uses. They have already been demonstrated as valuable raw materials for the manufacture of synthetic resins of the "Glyptal" type. The more recent patent literature suggests their use in conjunction with soap as wetting agents, and some of the ethers are further proposed as starting points in the preparation of new detergents as substitutes for soap. Urethane and nitrated derivatives of certain of the aryl ethers of glycerine have been investigated for medicinal purposes and as explosives. The latter are stated to be more stable than picric acid.

From a technical point of view at least the amines derived from glycerine are just as interesting as the ethers. Generally speaking they are very hygroscopic, viscous liquids or solids. They are strong bases with an ammoniacal odor. They combine readily with fatty acids to produce soaps which are soluble in organic liquids, and are excellent emulsifying agents. They have been used both to esterify natural resins and to produce nitrogenous "Glyptals" by reaction with polybasic acids. Some phenylurethane derivatives are stated to have anaesthetic properties.

Of the numerous possible oxidation products of glycerine, only a few have been studied to any great extent. Glyceric acid, tartronic acid, mesoxalic acid, and dihydroxyacetone are perhaps the better known. Chemical, electro-chemical, and biochemical oxidations of glycerine have been reported, but it is not believed that any of the work has had as its object the development and practical application of these derivatives. There is some evidence to indicate that these oxidations might be effected in a practical manner by air in the presence of catalysts. If the reaction could be controlled or limited to the desired products, interesting applications are potential rewards.

Biochemical syntheses have produced numerous products from glycerine which includes such compounds as ethyl alcohol, acrolein, hydroacrylic aldehyde, n-propyl alcohol, n-butyl alcohol, butyric acid, lactic acid, phorone, citric acid, and trimethylene glycol. None of these reactions, however, has appeared to have practical interest, principally because of more economic methods of production, of these compounds generally, by other means.

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