MANUFACTURE OF GLYCERINE IN INDIA.

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1. *What is glycerine:*

Glycerine or glycerol, to speak in terms of chemical phraseology, is a trihydric alcohol. It is usually found in combination with fatty acids in natural fats and oils. It has been the tendency to designate the name glycerine to the technically prepared pure substance which is the nearest approach to glycerol, represented by the formula, $OH . CH_2CH . OH . CH_2OH$.

2. *Sources of glycerine:*

Glycerine is a basic constituent of oils and fats, of which a large variety is available abundantly in this country. The approximate percentages of available glycerine in some of the important Indian oils and fats are given below:—

Cocoanut Oil	13·5%
Mhowa Oil	9·0%
Groundnut Oil	9·8%
Tallow	9·5%
Cottonseed Oil	9·8%

3. *Characteristics of glycerine:*

The British Pharmacopœia describes glycerine (glycerinum) as a clear, colourless, odourless, syrupy liquid, having a sweet taste, which is followed by a sensation of warmth. It is hygroscopic and is optically inactive and neutral to indicators. Its molecular weight is 92·06 and specific gravity (15·5°C./15·5°C.), 1·260–1·265.

4. *Manufacture of glycerine in India:*

The manufacture of glycerine in India is of recent origin, and is carried out at present only by two concerns, namely, the soap factories of Lever Bros. (India), Ltd. and the Tata Oil Mills Co., Ltd.* Until 1934, the glycerine consumed in India was entirely imported, and it was only in the end of 1935, when Lever Bros. started to manufacture soap on a large scale in Bombay that glycerine began to be produced in India. The Tata Oil Mills also put up about

* Since this article was contributed, two other plants have been set up in Bombay for the manufacture of glycerine.

the same time a Glycerine Recovery Plant at their Cochin factory for the manufacture of crude glycerine, which they exported to European markets successfully until 1939, when they erected a new and up-to-date Soap Plant in Bombay, where they laid down a Glycerine Distillation Plant for the manufacture of Pharmaceutical, Commercial and Dynamite glycerine.

5. *Import of glycerine into India:*

The imports of glycerine into India during 1931–36, *i.e.* 5 years prior to the starting of glycerine production in India, and from 1936 onwards, *i.e.* after Lever Bros. and Tata Oil Mills started manufacturing, are revealing:

Imports of Glycerine into India.

Year.	Cwts.	Value.
		Rs.
1931-32	7,687	2,65,070
1932-33	9,990	3,13,006
1933-34	11,855	3,76,743
1934-35	10,988	3,89,890
1935-36	9,838	4,27,746
TOTAL ..	50,358	17,72,455
Average per year .. .. Average rate per cwt.: Rs.35·20	10,071	3,54,491
		Rs.
1936-37	1,956	70,376
1937-38	1,628	1,07,015
1938-39	4,189	1,97,520
1939-40 (for 9 months only) ..	781	36,206
TOTAL ..	8,554	4,11,117
Average per year .. .. Average rate per cwt.: Rs.48	2,203	1,05,796

(*N.B.*—The above prices are c.i.f. Indian Ports, and to them will have to be added Import Duty at the rate of 25% *ad valorem* to arrive at the market prices.)

From the above figures it would appear that when Lever Bros. (India), Ltd. started making glycerine, they managed to reduce the imports substantially, and with the coming on the Indian market of Tata's glycerine in 1939, the imports had virtually ceased. This is a gratifying feature, as it has provided the country with a valuable commodity, the importance of which in wartime cannot be underestimated. India would have been in an unenviable position during the present time, when Europe is engaged in a ruthless war, if glycerine were not manufactured in the country. During the last World War, when India's requirements of glycerine were met from abroad, it is reported that the price of glycerine had gone up to as much as Rs.150 per cwt. Today, in spite

of the war, the price of glycerine in India is about Rs.62 per cwt., an increase of about 15% over the pre-war price. This increase was necessitated to cover the higher cost of chemicals, packing materials and labour which the war has brought about.

6. *The method of recovery of glycerine:*

The liberation of glycerine from oils and fats can be effected by several processes. The method adopted in India so far is to recover it from the spent lyes which are produced in the course of soap manufacture, by what is known as the 'Settled Process'. When oils are saponified with caustic soda by steam, the fatty acids present in the oil combine with the caustic to form soap. The soap is thereafter washed by a salt solution to free it from glycerine and other organic and inorganic impurities that are present in the oils saponified. On settling the mass, the soap floats, whilst the spent lye containing glycerine, salt and impurities is run down from the bottom of the soap pans to the glycerine recovery plant for purification and concentration. The glycerine content in the spent lye varies from as low as 4% to as high as 11%, depending upon the glycerine content of the raw materials employed in the manufacture of soap and the care and skill bestowed in the manufacture of soap and in the production of lye in relation to the weight of oils taken for saponification. Since glycerine is a by-product of the soap industry, the requirements of the soap boiler usually determine the choice of the oils and fats, and this in turn is conditioned by the cost and the soap-making qualities of the oils and fats used. The efficiency of glycerine recovery, therefore, depends to a large extent upon the thoroughness with which the washing of soap is carried out in the pan, as also upon the purity of the raw materials used, since the impurities present in the raw materials will necessarily find their way into the spent lyes.

7. *Availability of glycerine in India:*

The production of soap in India is estimated at about 90,000 tons per annum. Assuming that the major portion is made by cold and semi-boiled processes, the glycerine that ought to be available for recovery from the Settled Process of manufacture should work out to at least 2,500 tons per annum, but even this quantity is not produced, and the present production of glycerine in India is estimated at about 1,000 tons per annum. Unfortunately, in India the manufacture of soap by the Settled Process has not advanced rapidly enough due to the facility with which soap can be made by cold and semi-boiled processes which need little or no equipment, and which can, therefore, be made on cottage industry scale. With the recent attempts to revive village and cottage industries in India, the manufacture of soap on cottage basis is likely to get an impetus to the detriment of a valuable by-product like glycerine. Thus a good portion of the recoverable glycerine that is already running to waste will continue to run to waste on a still larger scale.

The cottage factories have neither facilities nor technical skill to make soap by the Settled Process or to evaporate the spent lyes. Even in small factories where soap is made by the Settled Process, the installation of glycerine recovery and distillation plant is not an economic proposition, and unless the soap industry in India is organised on a better basis (particularly if the small sized plants are made to realise the importance of working together) the recovery of glycerine by small factories will not be worth their while. As the demand for glycerine in India is likely to increase with the development of new industries, a larger production of glycerine can only be had either by the establishment in different parts of India of large size soap factories, capable of manufacturing soap by the Settled Process, or by getting the smaller soap factories to agree to send their soap lyes to large central glycerine recovery plants, or by the development of a new industry in India, viz. the manufacture of fatty acid by the splitting of oils. It may not be out of place to mention that on the one hand we are running to waste soap lyes which are rich in glycerine and on the other we are importing lakhs of rupees worth of pharmaceutical and toilet preparations in which glycerine is an ingredient in one form or another. The sales of imported pharmaceutical preparations in India are on the increase, whilst toilet preparations which are meant to enhance 'my Lady's' charm and complexion seem to be growing in popularity with the women of the country.

8. *Other methods of recovery:*

Before detailing the method of treatment and evaporation of the spent lyes for the manufacture of glycerine, it might be advisable to consider the three other methods which find favour for the recovery of glycerine. These methods are:—

(1) the Autoclave method,
(2) the Twitchell process, and
(3) the Fermentation method.

In the Autoclave process, the oils and fats are boiled with steam under pressures of 6 to 10 atmospheres, with lime, magnesia, zinc oxide or zinc dust, whilst in the Twitchell process, the hydrolysing agent is a special reagent named after its inventor Twitchell and the operation is conducted at atmospheric pressure. By these processes, a higher recovery of glycerine than from soap lyes is feasible, since in the manufacture of soap a certain amount of glycerine is always left over in the soap in spite of all the care and technical efficiency that can be brought to bear in its manufacture. But these two processes, however, have a serious disadvantage in that, during the process of splitting the oils, the resultant fatty acids are of a dark colour and cannot be used directly either in the soap or any other industry, unless distilled under a high vacuum. The third or the Fermentation method needs special consideration in India, as an enzyme isolated from castor seeds which are available

in plenty in India forms the hydrolysing agent in this process. This method has also a greater advantage over the other two processes, due to the fact that the capital outlay is comparatively small and the resultant fatty acids are sufficiently light coloured for direct use in the manufacture of soap. The only disadvantage with this process is the purification of 'Sweet Waters' which requires a little extra care and skill. With the industrialisation of India, and particularly with the growth of the cosmetic industry, the demand for a high quality stearine—a commercial mixture of stearic and palmitic acid, with a small proportion of oleic acid—is likely to steadily increase, and one or the other of these processes is therefore likely to be developed for the manufacture of stearine in India within the next few years. Mhowa and cottonseed oil, amongst other Indian vegetable oils, appear to be suitable raw materials for the manufacture of stearine, as they are rich in palmitic and stearic acids.

9. *Quality of spent lyes:*

It would be obvious that, if the evaporation costs are to be kept low, considerable attention must be paid to see that the spent lyes are rich in glycerine. Also, to keep the treatment cost within reasonable limits, the spent lyes should be free or very nearly free from caustic alkali, organic impurities, carbonates, etc. As stated earlier, a certain amount of impurities are inevitable in the lyes, as they are the impurities which are present in the oils and fats and which must necessarily find way into the lyes when soap is being washed with the salt solution. Again rosin (which forms an important ingredient in the composition of many grades of soap) with its impurities gets into the glycerine plant in spite of all care. Thus, when the spent lyes are transferred to the glycerine plant from the pan room, they contain, in addition to salt and glycerine, a small percentage of dissolved soap, other organic impurities, carbonates, etc. The efficient working condition in a pan room, however, will yield spent lyes with a high percentage of glycerine and free from, or containing as little as possible of, alkalis, carbonates, organic matter, etc.

10. *The treatment and evaporation of lyes:*

The treatment of lyes consists in removing the various impurities like carbonates, etc. from them. The treatment and evaporation of lyes are carried out under three distinct operations. In the first operation, the alkalis and most of the organic impurities are precipitated with the help of chemical reagents like aluminium sulphate or ferric chloride with hydrochloric acid. After treatment with three reagents, the lye is filtered and treated with caustic soda to remove the excess of aluminium or iron present. This is the second operation. It may be stated here that the comparatively high cost of hydrochloric acid, and therefore of ferric chloride also in India, acts as a great handicap in the treatment of lyes, and if they were available at a cheaper price, the use of aluminium sulphate could be completely dispensed with,

since this reagent ultimately reduces the purity of the salt recovered and thereby affects the efficiency of graining of soap. It should also be borne in mind that the chemicals used, particularly the acids, should be absolutely free from arsenic and lead, as once the impurities are introduced in the system, it is difficult to get rid of them during any subsequent stages. The stringency of the B.P. specification for chemically pure glycerine regarding arsenic and lead can be judged from the following stipulations laid down:—

Limit for arsenic: 4 parts per million.
,, ,, lead: 1 part per million.

The treated and purified lyes are now ready to be taken into the evaporators for the third and final operation. In the earlier days, it was the practice to evaporate the lyes on open hearths and to concentrate them up to about 80% glycerine content. With the introduction of vacuum evaporators, great economy in recovery as well as fuel consumption has been effected in the concentration of lyes, and today evaporators ranging from single, double and multiple effect are in use for the concentration and evaporation of lyes. The popular type is the double effect evaporator, in which stepping up the vacuum in one of the vessels enables the vapours from the other to be economically used for purpose of evaporation. As the major part of the water present in the lyes evaporates, the salt from the lyes settles out and is collected in special salting-out boxes fixed to the bottom of the vessels. The evaporation is continued till the glycerine content in the lye reaches about 80%, and this product constitutes the 'crude' glycerine of commerce. This crude glycerine contains 80% glycerol, 8–10% salt and 1–3% organic impurities with a little water.

11. *Distillation of crude glycerine:*

The crude glycerine is distilled in a separate distilling unit for the production of industrial pale straw, dynamite, C.P. and other qualities of glycerine. Pure glycerol boils under atmospheric pressure at about 290°C., whereas at lower pressures it distils at lower temperatures. A higher vacuum, however, gives an improved product and this point has received merited attention in the design of modern plants. The modern tendency is to distil with the aid of superheated steam under a very high vacuum of 6 to 9 mm., which would permit of distillation below 200°C. By suitably adjusting the temperature of the condensing vessels, pure glycerine is condensed and recovered. On distilling the 80% crude, a product of a pale yellow colour is obtained as the first distillate. This product contains 99 to 100% glycerol and has a sp. gr. of 1·262 to 1·265. This constitutes the dynamite or the industrial pale straw glycerine of commerce. By further distillation and purification (by means of bleaching carbon), chemically pure glycerine satisfying the rigid specifications laid down in the British Pharmacopœia is obtained. The final glycerine as it comes out from the distillation plant is then packed in tins or galvanised

drums and is ready to go out to the market. A large amount of care is necessary in the process of distillation, particularly with regard to the removal of free fatty acids. Although the British Pharmacopœia has not laid down any limits with regard to the presence of free fatty acids, it has been found in practice that to produce an odourless glycerine, the limit of free fatty acids should not be above 0·01%, as otherwise they give a smell to the glycerine which is considered objectionable. With judicious care in the treatment of crude glycerine, as also in the process of distillation, the trouble regarding the presence of free fatty acids can, however, be easily overcome.

12. *Foots:*

In the process of distillation, a certain tough plastic substance is left in the still as a residue, which is known as 'foots'. The dry foots on analysis are found to contain about 60% of ashes mainly composed of sodium chloride and sodium sulphates. The balance of 40% consists of a mixture of glycerol and condensation products of glycerine, such as poly-glycerols. The use to which the foots can be put has remained a tough problem and awaits a solution by research chemists.

13. *Uses of glycerine:*

The following properties of glycerine will give an insight as to its possible use in the various industries:—

(*a*) It has a sweet taste.

(*b*) It is highly hygroscopic and on exposure to the atmosphere, takes up as much as 50% of its weight of water.

(*c*) It has powerful solvent properties, and when mixed with water, improves the solvent property of the latter.

(*d*) It acts as an antiseptic even in dilutions up to about 12%.

The largest use of glycerine ordinarily in India is in the pharmaceutical industry and medical stores, and to some extent in the manufacture of toilet preparations; but since the beginning of the war, it finds a ready and larger application in the production of dynamite and other explosives for defence purposes. Today perhaps its important consumer is the explosive industry, next to which comes its use in the pharmaceutical industry. Many tonics, wines, liquors, contain glycerine because of its smoothening, sweetening and preservative properties. In the tobacco industry, it is used to keep the tobacco moist, sweet and also to act as a partial antiseptic. In toilet preparations and cosmetics, it finds extensive use, as it imparts to the skin 'brilliance, softness and delicate colour'. Its hygroscopic nature is taken advantage of for keeping articles soft and pliable and also to prevent their drying up. It is used for keeping wood, leather, paper, etc. soft and pliable and also for keeping moist, copying and printing inks, blacking, etc. Due to its high solvent action, it is used as a solvent in extracting perfumes and alkaloids.

14. *Other possible uses :*

There are one or two directions in which the use of glycerine can be extended in the Indian market. In the textile industry, large quantities of 'wetting' agents are in use for keeping the fabrics of cotton threads in the moist condition. Judicious use of glycerine in such preparations should find increasing favour with mill technicians. In tobacco curing, jaggery water seems to be in use for preserving the moisture in the leaf. Here also glycerine can very advantageously be used. In these instances, a proper guidance in the use of the right article for the right purpose is all that is needed.

15. *Post-war problem :*

When the present World War II ends, the problem of finding new uses for glycerine will be of increasing importance, and an opportunity presents itself to research chemists to work from now onwards in finding ways and means for using glycerine in different industries for different purposes. The existing limitation of demand will soon serve as a check on a larger production of glycerine. It is in the interest of the Indian industries in general and the glycerine industry in particular that steps should be taken to tackle these various problems. Recent patent records and industrial magazines refer to various uses of glycerine. This information should be made the basis for conducting further investigations for evolving new uses for glycerine to suit Indian manufacturing conditions.