

Costa Rica 1, Mexico 2, Panama 2, Uruguay 1, United States 88 (10 of which are located in the United States possessions), Trinidad 1, Tobago 1, Andaman Islands 2, Burma 1, Hong Kong 1, China 5, Hawaii 5, Japan 2, Dutch East India 5, Russia in Asia 1, Egypt 2, Morocco 2, Mozambique 2, and Tripoli 1.—Canadian Engineer.

THE UTILIZATION OF WASTE INDIA RUBBER.* By WALTER F. REID, F.I.C.

To the chemist there is in reality no waste; it is simply a matter of expediency whether and in what way any substance shall be utilized. The waste product of one industry forms the foundation of subsidiary industries, and it not infrequently happens that the by-product replaces its parent or becomes the mainstay of the manufacturer. In this connection, some of us can still remember the time when coal tar was an objectionable by-product, difficult and costly to dispose of; the chlorine products of the Leblanc soda process render competition with the ammonia process possible, and we have explosives manufacturers erecting soap works for the sake of the glycerine which was formerly poured down our sewers in enormous quantities. It is, in fact, a rare occurrence that a new industry is started without the production of some by-product for which a use has to be found.

It is not often that the industry producing the by-product is the only outlet for its own waste, as is the case with india rubber. In this instance, practically the whole output becomes, sometimes in a very brief space of time, a waste product. In some cases, as with motor-car tires, mechanical deterioration takes place long before chemical changes cause disintegration; but in others oxidation of the material renders it unfit for its original purpose.

For many years, especially while abundant supplies of crude rubber were obtainable at moderate prices, little attention was paid to waste rubber, although as early as 1846 it was recognized that such waste might be utilized with advantage, and Parkes laid the foundation of the alkaline method of recovery. Of late years, however, there have been remarkable developments in the india rubber industry. The increased demand, mainly due to electrical progress and improved methods of locomotion, has more than equaled the immediately available sources of supply, and the result has been a considerable increase in price. The total production of rubber last year was about 68,000 tons, and the increase in the annual output has been about 15,000 tons in five years. As bearing upon the quality of the material, it will be interesting to ascertain the chief sources of supply. America easily leads the way with a production of 42,800 tons, of which 41,000 tons, or nearly two-thirds of the whole quantity harvested, is credited to Brazil. Much has been said and written lately about the production of rubber in Mexico, and considerable amounts of American capital have been invested in "Guayule" rubber; but last year the whole production of Mexico only amounted to 200 tons, so that the quantity of this low-class rubber is not yet of importance. It has been calculated that only about 300,000 tons of the shrub "parthenium argentatum" from which "Guayule" rubber is extracted are available, and, with a yield of 6 per cent of rubber, this quantity would only produce about 18,000 tons of rubber.

Africa comes next as regards quantity, the output being 23,400 tons. The Congo Free State is here the largest producer, having brought 4,500 tons into the market. In view of the methods by which this rubber is obtained, it can scarcely be expected that the production will be materially increased in this district. Germany is devoting much attention to rubber in her African colonies, and will soon be producing plantation rubber.

The rubber derived from Asia and Polynesia is estimated at 1,800 tons per annum; but this quantity will probably increase rapidly within a few years, and no doubt "plantation" rubber will in time displace "Para" from its premier position as regards quality. Some of the rubber sent to us from plantations in the East is of excellent quality, quite equal to the best "Para," and very free from impurities; but many of those who grow the rubber are not sufficiently informed as to the requirements of the user, and there is here a wide field for the trained chemist, as compared with the chemical inventor who has not been trained. It is estimated that trees already planted should, in about ten years' time, yield some 25,000 tons of rubber per annum; but too little is known of the influence of climate, soil, and diseases of the trees to make this a reliable estimate.

The great bulk of rubber produced is of good quality, and, if it went into consumption in the state of purity in which it is received by the manufacturer, the average quality of the waste would also be high. Unfortunately, however, substances of the most varied properties are added during the process of manufacture. Mineral matters of various kinds sometimes make up the greater part of the weight of what is sold as india rubber, while the rubber itself is largely replaced by substitutes, generally consisting of some form of solidified oil. One ingredient, however, is common to nearly all forms of manufactured rubber, and it is this that has proved the stumbling block to most inventors who have endeavored to utilize rubber waste. I refer to the sulphur used in vulcanizing, part of which enters into chemical combination with the rubber, and which is very difficult to expel again without injuring the quality of the material. Vulcanization is at present a

necessity, for no other process has yet been discovered which renders rubber so inert to changes of temperature. Once the vulcanization has taken place, however, the cut surfaces of rubber will no longer adhere to each other, and the material cannot be worked into a homogeneous mass. It is probably the sulphur that is the cause of the disintegration of rubber, because crude rubber will keep for a number of years without deterioration. Here is a piece of crude Para rubber sixty-five years old. It was bought in Glasgow in 1842, weighs one ounce, and cost 2s. 6d., and is practically in the same state now as then. The other piece of raw rubber came into my possession in 1861, and is also in quite good condition. The best sample of vulcanized rubber I have met with is a red rubber stopper now twenty years old; but, as you will observe, it has become quite brittle outside, although still soft inside. Nearly all old vulcanized articles contain traces of sulphuric acid, due to the gradual oxidation of the free sulphur, and this is probably the main cause of the deterioration. Rubber which has become brittle through age cannot be regenerated by any of the processes at present in use, and is practically valueless. In many cases, however, rubber articles have to be discarded long before chemical disintegration sets in. Motor-car tires and shoes are worn out by attrition, sometimes in a very short time, and yield valuable material for the industry we are discussing. The inner pneumatic tubes of bicycles and motor cars are the best waste available on a large scale; but, as they can be utilized by grinding and mixing with fresh rubber without undergoing any chemical process, they command a relatively high price. Manufactured rubber contains mineral matters of various kinds, known as filling materials or compounding materials. The most frequently used are calcium carbonate, calcium sulphate, magnesium carbonate, magnesia, barium sulphate, zinc oxide, litharge, white lead, china clay, French chalk, and lithopone.

In regenerating rubber, it is not necessary to remove all of these; but their presence naturally diminishes the value of the product obtained. Perhaps the most troublesome impurity in rubber waste is fiber derived from the fabrics which so frequently form the basis of rubber goods. In a motor-car tire, for instance, there may be eight or ten thicknesses of fabric in about half an inch. The best method of removing fiber is the mechanical one, as this does not deteriorate the quality of the rubber. The whole mass is ground into a coarse powder which is then exposed to a current of air by means of which the fibers are removed, and the rubber is left behind. The separation is only partial; but the removal of the fiber is generally complete enough for practical purposes.

There are, however, some materials in which the fiber is so intimately incorporated with the rubber that it cannot be separated by mechanical means. In such cases, the grinding is continued until the fiber is reduced to a powder which remains in the recovered rubber, or the fiber is destroyed by chemical means. The chemical reagents used differ according to the nature of the fiber. Vegetable matter is destroyed by treatment with an acid, generally sulphuric acid, or an acid salt, followed by heating. The decomposed fiber can then be washed out, together with such mineral matter as is soluble in the acid used. For the destruction of animal fiber, such as wool, an alkaline solution is preferable, followed by drying and subsequent washing. Although india rubber is less acted upon by both acids and alkalis than the fibers with which it is mixed, yet there is always sufficient action to deteriorate considerably the quality of the recovered product. Innumerable attempts have been made to recover rubber by dissolving the waste in a suitable solvent; but most of these have failed, owing to the fact that vulcanized rubber becomes insoluble in the usual solvents for raw rubber. It will swell in many liquids; but will not dissolve until such a degree of heat is applied that the rubber itself is decomposed. Vulcanized rubber can be converted into a homogeneous mass by superheating; but this causes a decomposition of the rubber itself, and, although the product can be used in admixture with fresh rubber, and has even great cementitious powers, it is very deficient in elasticity and tensile strength. Many of the varieties of recovered or regenerated rubber in the market are in reality overheated, while some are overworked.

There are many liquids which will lixiviate part of the free sulphur from the vulcanized material; but in most cases their use involves a permanent deterioration of the rubber, which still retains the bulk of the free and practically the whole of the combined sulphur.

Last year M. A. Tixier, a French chemist, made the interesting observation that vulcanized rubber was completely soluble in terpineol. Upon this fact, a process for the regeneration of waste rubber has been based, the patent specification for which was recently published. (Fr. Pat. 370,619, October 19, 1906.) The rubber, whether vulcanized or not, is reduced to pulp and digested with twice its weight of terpineol in a closed vessel fitted with an agitator. The temperature specified is 100 deg. to 150 deg. C. The solution thus obtained is agitated with four times its volume of benzene. Insoluble impurities subside, the clear liquid is decanted, and the benzene distilled off. The rubber is then precipitated by the addition of alcohol or acetone. Regenerated rubber obtained in this way resembles the natural product more than any other kind that I have seen. It is very viscid, and will sand a large admixture of neutral mineral substances. It can be revulcanized and possesses considerable power of resistance to chemical reagents. This latter quality is

probably due to the fact that the method of preparation eliminates the resinous impurities of the rubber which are most readily attacked by acids or alkalis.

In spite of the poor quality of the rubber recovered by the old processes, the trade in this article is considerable, especially in the United States. No less than 10,600 tons of waste rubber was imported into that country last year. The recovered rubber exported amounted to 380 tons, of which Great Britain took 211 tons. Our home production of recovered rubber is considerable, but official statistics are not available.

Waste rubber is sorted into about a dozen different grades, which vary in price according to the quality of the rubber which they contain and the greater or less difficulty of extracting.

BACTERIA IN CHEESEMAKING.*

By PROF. HERBERT W. CONN.

IN regard to the relation of micro-organisms to cheesemaking, we know as yet less than about their work in buttermaking, and the practical applications have hitherto not been extended. It is certain that the relation of bacteria to many problems of cheese ripening is very intimate, and that further studies will disclose facts that we do not now know. It is, also, fairly certain that practical applications of bacteriology to cheesemaking are sure to come, and many phases of this industry are to be modified in the not far distant future by new discoveries. Already some practical results have been obtained, and the present time is seeing a large knowledge both obtained and practically applied to cheesemaking.

There are many different kinds of cheese, and no two types are made in the same way, have the same history, or are ripened by the same agents. Each special kind of cheese has to be studied by itself, and it is difficult to make any general statement concerning the relation of micro-organisms to cheesemaking. Moreover, it is quite certain that some of the phenomena of cheesemaking and cheese-ripening concern other factors besides the growth of bacteria or similar agents, and we do not, as yet, know to what extent cheese-ripening is due to the growth of micro-organisms. A few facts, however, are now well proved and may be briefly summarized.

The relation of bacteria to cheese, if they have any relation at all, is to the phenomena of the ripening of the cheese. The green curd, when first made into a cheese, has no cheese flavor, is hard and tough, and, in general, not an appetizing product. It is, however, ripened for a varying period, during which time the chemical nature is undergoing changes, and the cheese becomes more easily digestible and changes its flavor. It is the latter fact, the change in flavor, which is of the highest importance in rendering cheese a favorite market product, and in which in all probability micro-organisms are in some degree concerned. As yet, however, we do not in many cases know to what extent cheese flavors are due to the action of bacteria.

It is certain, however, that in nearly all types of cheese the first phenomenon which occurs, and which appears to be quite necessary to all subsequent ripening, is the souring of the curd. We have already learned that this development of lactic acid is dependent wholly on the growth of bacteria; hence, the first process of cheese ripening is bacteria growth. For this reason, it has become evident that to make a high-grade type of cheese, it is necessary that the milk should contain a sufficient quantity of favorable lactic bacteria. We have already learned that there are two types of bacteria which produce lactic acid, one producing gas, and the other producing no gas. Cheesemakers have learned to their sorrow that the presence of gas-producing organisms, in any considerable quantity, is fatal to the production of a good quality of cheese. Great quantities of cheese are entirely spoiled by the growth of the gas-producing organisms. These facts have been appreciated only in recent years, and now cheesemakers are adopting various methods of checking the growth of gas organisms. Among other methods there is now being more and more widely adopted the use of pure cultures of lactic germs, to be added to the milk for the distinct purpose of controlling the souring as a preliminary to cream-ripening. Cheesemakers are to-day learning to control their ripening by the purchase of lactic cultures from dealers, and their inoculation into milk. This method has been developed in the last few years and seems likely to continue to extend widely. The inoculation of a large quantity of lactic bacteria helps greatly in holding in check the development of the gas-producing organisms, as well as of other bacteria which might produce trouble. Here, then, is the first practical application of bacteria to cheesemaking.

IN EDAM AND SOFT CHEESES.

It is interesting to note that even before bacteriologists understood facts concerning the relation of bacteria to cheese there had been made a practical application of the bacteria to the manufacture of one variety, the well-known Edam cheese of Holland. For quite a number of years it has been known that the manufacture of this cheese could be hastened and rendered more uniform by the use of a starter added to the milk, known as "slimy whey." This is a whey or milk in which certain species of bacteria have developed until there has been produced a decided sliminess. An addition of a proper quantity of this starter to the milk results in a decrease in the time of ripening of the cheese, and in a somewhat greater uniformity in the product. There is no improvement in the type of

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* The Country Gentleman.