BRITISH PHARMACEUTICAL CONFERENCE LONDON, 1953

REPORT OF A SYMPOSIUM ON CONTAINERS AND CLOSURES

AT the Symposium Session the Chairman, Dr. G. R. Boyes, presided, and introductory papers were read, in abstract, by Miss Violet Dimbleby, Mr. James Haworth, Mr. D. Stephenson, and Professor H. Berry.

For Miss Dimbleby's address see The other papers are printed below in abridged form.

THE TECHNOLOGY OF RUBBER

BY JAMES HAWORTH, B.SC., A.R.I.C., A.Inst.P.

J. G. Ingram and Sons, Ltd.

INTRODUCTION

IN spite of continuous contact between rubber users and the manufacturer since 1822, when Thomas Hancock was covering corks with rubber to improve their sealing properties, many misunderstandings have existed between the two parties. The causes of these appear to be twofold. In the first place, while rubber has found a wide range of application owing to its remarkable properties, little is really known of the basic physics and chemistry of its structure and properties. Empiric methods rather than scientific techniques play the major part in dealing with problems arising in the use of rubber. Secondly, owing to the fact that rubber technology is more an art than a systematised science, much of its terminology lacks the precision of more scientific techniques. The use of the word "rubber" for a wide assortment of materials including raw rubber of many botanical species, the infinite number of vulcanised rubbers of varying composition and the newer synthetic rubbers, illustrates how even the key word of the industry can confuse.

The basic raw materials of rubber technology are materials possessing properties intermediate between solid and liquid whose behaviour cannot be explained by laws appropriate for either ideal solids or liquids. Since the properties of the materials can be moved over the range between the ideal states, showing under some conditions properties akin to a liquid and under others more characteristic of a solid, it is perhaps not suprising that many perplexing results are obtained in service.

WHAT RUBBER IS

Natural Rubber.

Raw rubber is obtained as an aqueous dispersion (rubber latex) which exudes from the trunk of the tree when shallow cuts are made in the bark. Rubber latex contains 30 to 45 per cent. dry rubber and is subject to some considerable variation as is usual with materials of botanical origin.

The dried raw rubber, prepared by coagulation of the latex, consists of about 90 to 93 per cent. of a hydrocarbon of empirical formula C_5H_8 having an unsaturated double bond to each unit of C_5H_8 which are linked together in the *cis* position to form long chains[1]. The remainder of the raw rubber consists of resins to an extent of about 3 per cent. and between 2 and 3 per cent. of sugars and proteins.

In spite of all the work which has been carried out on the non-rubber components, there is not as yet, a full understanding of the part they play in modifying the properties of raw rubber.

Raw natural rubber as used in industry is of two main types. The essential difference between them arising from the methods of converting the wet coagulum to the dried sheet. The type used in greatest quantity is smoked sheet rubber. This is prepared by drying the washed coagulum over the smoke of wood fires when phenolic bodies in the smoke are absorbed which, besides colouring the rubber a brown amber shade, act as inhibitors of mould growth during storage. Smoked sheet rubber has always a characteristic odour which persists into the final vulcanisate. The second type, pale crepe rubber is washed more thoroughly than other grades and so tends to contain less non-rubber material. Sodium bisulphite is added to this grade during preparation to preserve the pale colour and inhibit mould growth, drying being carried out at or near atmospheric temperature in air.

Synthetic Rubber.

While the synthetic rubbers are similar in molecular structure to natural rubber, their often very great differences in chemical composition give rise to important differences in properties. Most synthetic rubbers resist heat and oxidation better than natural rubber, while some show remarkable inertness to the swelling effects of oils which so readily attack natural rubber. They are usually more difficult to process than natural rubber and tend to crystallise at much higher temperatures. Types used include polymers of chloroprene valuable for oil and light resistance, silicone polymers which have great heat resistance as well as copolymers of butadiene with styrene, *iso*butylene with isoprene and butadiene with acrylonitrile.

The synthetic rubbers nearly all contain added chemicals which act as stabilisers during storage. These include phenyl β-naphthylamine in some butadiene/styrene rubbers, while, in the chloroprenes, sulphur compounds such as thiuram disulphides are used.

The Properties of Raw Rubber

· Raw rubbers exhibit a marked variation in physical properties with temperature. At low temperatures they become stiff and hard in the so-called frozen state. As the temperature increases they soften and become flexible, while at higher temperatures, they become plastic rather than elastic so that any deformation under stress becomes permanent.

From the standpoint of solubility, rubber is a liquid. This may seem

surprising, but a study of the mechanical properties indicates that the molecules of the rubber structure are free to slip past one another[2], the characteristic of the liquid state. The absorption of liquids and solids by rubber can thus be regarded as the mixing of two liquids or the solution of a solid in a liquid. Gee[3] has shown that in many cases, liquids and rubbers with the same cohesive energy density will mix to the greatest extent and the degree to which a liquid will mix with a rubber is related to the difference between the cohesive energy densities of the two. Many exceptions to these relationships occur, so that for practical purposes the extent to which a given liquid will be absorbed by a rubber can only be determined by experiment. Large and unexpected effects are known to occur when rubbers are subjected to contact with mixtures of liquids.

The absorption of water by natural raw rubber is influenced mainly by the amount of non-rubber constituents present. Specially purified rubbers with low non-rubber content absorb very little water[4]. There is little systematic information on the properties of synthetic rubbers in relation to this property. Silicone rubbers appear to be fairly resistant[5], while *iso*butylene rubber has been found to show less water absorption than butadiene/styrene[6].

Raw rubbers are permeable to gases to varying degrees dependent on the rubber type and the gas. The permeability of natural rubber to oxygen being about 12×10^{-8} c.c./sec. at 63° F., for a test specimen 1 cm. thick and 1 sq..cm. in area under a pressure of one atmosphere. The process involved appears to be a function of both solubility and diffusion[7].

The chemical properties of the raw rubbers are determined essentially by the constitution of the unit in the polymer, the double bonds in the hydrocarbon chains of many of the rubbers being the main point of reaction. The most important reaction is with sulphur which is the basis of the process known as vulcanisation or cure. The process is usually considered as the formation of cross links between the long chains in the structure with a consequent depression of plastic and liquid properties[8] and enhancement of elastic properties.

The second important reaction is one that occurs spontaneously with oxygen of the atmosphere and also involves the centres of unsaturation in the polymer. This causes a breaking up of the hydrocarbon chains and ultimately all rubber-like properties are destroyed. In spite of the loss of some saturation accompanying vulcanisation, the vulcanisate is even more subject to oxygen attack than raw rubber. It is considered that this is due to the possibility of attack at the sulphur bridges. The process is catalysed by light, heat and traces of certain metals such as copper.

The ready reaction of many rubbers with halogens is also a consequence of centres of unsaturation in their structure.

THE RUBBER COMPOUND

The essential composition of the majority of rubber articles is the "rubber compound" made up of raw rubber with selections from a wide range of materials chosen to serve either or both of two purposes, viz. :—

(1) To facilitate manufacture.

(2) To control the ultimate physical and chemical properties and service behaviour of the rubber article.

In spite of the fact that many of the ingredients have effects other than the one intended, which results in every rubber compound being a compromise between competing claims, it is possible to classify them according to their main function in the rubber compound[9]. Table I illustrates the main types of compounding ingredients with typical practical examples.

TABLE I

Classes of ingredient	Soft vulcanised rubber	Ebonite	Synthetic rubber
Rubber	100 Raw natural rubber	100 Raw natural rubber	100 Chloroprene
Vulcanising agent ..	2 Sulphur	45 Sulphur	} 10 Zinc oxide } 4 Magnesia
Activator	} 1 Stearic acid } 4 Zinc oxide		
Accelerator ..	0·75 Diphenylguanidine	2 Aldehyde amine condensate	
Extending filler ..	60 Whiting		
Reinforcing filler ..	75 China clay		30 Carbon black
Softener	1 Mineral oil		7 Tricresyl phosphate
Antioxidant ..	1 Phenyl β-naphthyl-amine		1 Phenyl β-naphthyl-amine
Pigment	5 Iron oxide		
Special components	3 Paraffin wax	3 Cotton seed oil	

COMPOUNDING NATURAL RUBBER

Vulcanising Agent.

The essential ingredient in all rubber mixes after the rubber has been selected, is the vulcanising agent which is usually sulphur. In order to show a marked improvement over uncured rubber by treatment with sulphur it is necessary to mix into the raw rubber about 8 per cent. of sulphur and heat the mixture for as long as 6 hours at 300° F. Consequences of the process include an increase in tension strength, stiffness, improved resistance to changes in temperature and decreased solvent solubility. The simple vulcanisation process has, however, a number of limitations. Resistance to oxidation is bad since the process of heating for a long time causes chain scission. Further, since the non-rubber components markedly influence rate of reaction with sulphur, variability due to differences in rubber quality is reflected in the quality of the vulcanisate.

Activators.

Early experience in use of the vulcanisation process soon showed that inclusion of some metallic oxide in the compound had a beneficial effect. Since it was shown that fatty acids occurring naturally in the raw rubber played such an important part in the process, a small amount of stearic or other fatty acid is added to the mix to swamp variations due to changes in amount of naturally occurring acid present. Metallic oxides, used as activators, include litharge, zinc oxide, lime and magnesia of which zinc oxide is most common.

Accelerators.

Accelerators have the effect not only of markedly increasing the rate at which vulcanisation takes place, but also of allowing a surprising degree

of control over the physical properties. It has become possible by the use of such compounds so to reduce the time of heating to bring about proper vulcanisation that factors such as thermal conductivity have become serious obstacles to obtaining uniform vulcanisation in the fastest curing mixes. Other consequences of the use of accelerators include reduction of the amount of sulphur in the mix and with particular types the vulcanising temperature can be lowered considerably.

Accelerators in general use include guanidines, e.g., diphenyl guanidine, di-o-tolyl guanidine; aldehyde-amine condensates. Many accelerators are derived from carbon disulphide of which the most common types are thiazoles, e.g., 2-mercaptobenzthiazole, thiurams, e.g., tetraethylthiuram disulphide and dithiocarbamates, e.g., zinc diethyl dithiocarbamate. The amount of accelerator (usually from 0·5 to 1·5 parts to 100 parts of rubber) added to the rubber not only effects the rate at which vulcanisation proceeds, but has a marked influence on the physical properties of the vulcanisate.

All the properties of a vulcanised rubber compound vary with the time of vulcanisation, some changing continuously without inflection, while others pass through a maximum or minimum value. The process of vulcanisation can be followed by such changes in properties and it is a regular practice to use tension strength as a means of fixing the best time of cure. Many of the properties which change with time of vulcanisation do not reach their optimum values at the same time so that when times of heating have to be chosen to give the best service properties choice is often a matter of compromise. If the amount of free sulphur left in the compound is excessive, it will tend to migrate to the surface on storage forming a characteristic white or yellow film often noticed with compounds of the older high sulphur containing type. When it is necessary to have a very low amount of unreacted sulphur in the compound, use is made of high dosages of tetramethylthiuram disulphide as an accelerator without the addition of elemental sulphur. Such compounds are often referred to as sulphurless compounds. As the time of vulcanisation increases the rubber shows less liquid properties and thus is decreasingly affected by liquids[10] which act as solvents. Water absorption is also reduced[11,12].

Accelerators have important side effects which influence their choice in particular applications. Many can cause changes in colour of the vulcanised rubber[13], and other effects of importance include taste, odour and toxicity. Some are not greatly affected in respect of their chemical structure by the vulcanisation process and thus, if used in large amounts, can migrate to form objectionable surface blooms on the rubber surface. Extensive use is made by the rubber industry of mixtures of accelerators to obtain special effects.

Fillers.

Fillers are added to the rubber compound to modify such properties as hardness, tension strength, stiffness of the raw compound and resistance to abrasion. They also influence such properties as liquid absorption and permeability to gases. The effect of the filler, added to the rubber as a

finely divided powder, depends on the size, shape and surface properties of the particles. It is considered by some authorities that the more active fillers do actually combine in some way with the hydrocarbon chains of the rubber structure producing an effect on the raw rubber similar to that obtained by vulcanisation. The fillers of this type are known as reinforcing fillers, they include carbon black, clays, magnesium carbonate, and zinc oxide. Extending fillers can be added to the rubber in varying amounts without detracting seriously from the tensile properties. These are used to facilitate manufacture owing to their influence on the plastic properties of the raw compound, and to control hardness and cut resistance and to reduce cost. Typical examples include barytes, whiting and talc.

Softeners.

Softeners are used to facilitate the processing of the raw compound and control the final hardness of the vulcanisate. In compounds based on synthetic rubbers which are prone to crystallisation at higher temperatures than natural rubber they also serve to depress the freezing temperature. Raw natural rubber can be softened by mechanical working in the presence of air or by heating; the process adversely affects resistance to oxidation in service. Many oils such as pine oil, petroleum or coal tar fractions and pine tar when added to the rubber bring about softening and also facilitate the incorporation of fillers. In synthetic rubber compounds, esters are used as softeners, such materials as dibutyl phthalate and dibutyl sebacate not only soften the compound but improve such properties as resilience.

Antioxidants.

It has been mentioned that vulcanised rubber is readily attacked by oxygen. Both heat and light accelerate the effect and since the reaction is autocatalytic, a very small amount of oxygen can produce a very marked deterioration in properties. The detailed behaviour of a vulcanised rubber in this respect depends markedly on the ingredients in the compound, the method of processing and the manner and degree of vulcanisation. The chemicals which are effective in slowing down the rate of deterioration are known as antioxidants and are normally used in amounts of the order of 1 per cent. on the rubber content of the compound. Types in general use include secondary aromatic amines, aldehyde or ketone/amine condensates and phenolic derivatives. Important side effects which influence antioxidant choice for particular applications include the tendency of some types to migrate and form a surface bloom while others cause marked changes in colour when the rubber is exposed to light[13].

Pigments.

Pigments used to obtain coloured effects include oxides of iron, sulphides of antimony and cadmium selenides and sulphides. Organic pigments are being used in increasing variety.

Special Ingredients.

Special ingredients used in the rubber compound serve a number of purposes. Paraffin and other waxes are widely used because of their

tendency to migrate to the rubber surface and so form a physical barrier over the rubber against oxygen attack. They also help to reduce water absorption[14]. Other ingredients used include tack producers, such as wood rosin, to enhance surface stickiness, stiffeners such as *p*-amino phenol as well as blowing agents for sponge manufacture.

The synthetic rubbers are compounded in a similar manner to natural rubber. There are, however, a number of notable differences. The former are usually more inert than natural rubber, vulcanisation is more difficult necessitating higher accelerator dosages and longer times of vulcanisation. They are usually much tougher in the raw state than natural rubber so that softeners are nearly always necessary to facilitate processing.

MANUFACTURE OF RUBBER ARTICLES

The essential processes of manufacture of articles for closures consist of:

(a) The mixing of the rubber compound;
(b) Formation of blanks of a suitable shape for loading the mould;
(c) Moulding and vulcanising;
(d) Trimming the moulded article.

The process of mixing and moulding has been admirably described in a form well suited for those not well versed in the art[15,16]. There are, however, one or two points worthy of mention as these have some bearing on the application of rubber to the manufacture of closures. The essential processes of mixing, forming and moulding the rubber all necessitate some treatment of the surface of the compound at each stage to prevent surface adhesion of the various raw rubber parts and to facilitate opening of the mould and removal of the finished article when vulcanisation is complete. It is usual to dust the raw compound with zinc stearate or french chalk prior to moulding to reduce surface stickiness. Use of gross excess can leave some material loosely bound to the surface and this can be easily dispersed in solutions coming in contact with it.

Mould release agents are always likely to be left on the surface of the rubber as a film. This is a very common cause of turbidity in solutions coming into contact with rubber articles.

Variations in the quality of the vulcanisate which arise from the processes of manufacture include variations of hardness and of other physical properties. These arise from variations in, the time and efficiency of the mixing operation, the times and temperature of vulcanisation, and the time of storage of the rubber compound between each stage of the process. The length of time between that of manufacture and that of testing can be of importance in this connection.

SPECIFICATIONS

The question of devising specifications[17] for vulcanised rubber articles is difficult and is often a source of great difficulty between users and makers of rubber articles. The main contribution that can be made by the pharmacist is one of accurate specification of requirements.

The main difficulty in drawing up a specification for a rubber article is

that the preliminary operations through which the rubber is put in the process of manufacture are "remembered" in the cured products. Hence identical compositions cured in the same way can have very different properties arising from variations in the processes through which they have passed. Specification of a rubber article by detail of the composition and final properties would thus involve the specification of both the methods and machinery of manufacture.

Attempts at basing specifications on chemical tests are also fraught with danger. For example, an acetone extract clause designed to prevent the use of rubber diluents could prevent the necessary inclusion of an antioxidant or softener in the formula. Of physical tests, tension strength is perhaps too freely used by the rubber manufacturer as a criterion of quality.

Accelerated tests intended to give information to be expected from the article in service can be misleading. For example, the very beneficial effects conferred on the rubber vulcanisate by inclusion of an antioxidant in the compound as shown by ageing tests conducted in oxygen under pressure at an elevated temperature are rarely as marked under natural conditions of ageing.

The most useful guidance which can be given to the manufacturer of rubber articles for use in pharmacy is to indicate the type of ingredients likely to cause trouble in service, so that these, if possible, can be excluded from the compound. More attention will have to be paid by both users and makers to the properties of rubber in contact with liquids and the formation of extractable matter by water and other fluids. Some consideration will have to be given to the possibility of the rubber absorbing materials from solutions in contact with them as well as the susceptibility of some rubbers to react with oxidising and halogenating agents.

Physical properties meriting attention include hardness and modulus which can influence resistance to piercing by needles, while tear resistance, compression set and gas permeability are of importance. Resistance to sterilisation procedures is of importance and the possibility of absorption in the rubber of phenolic disinfectants which can cause softening and surface stickiness should be considered. Some note of the change in properties over long storage periods will have to be taken and provided against when necessary.

FUTURE TRENDS

It seems likely that with the increasing understanding of the properties of rubber-like materials due to the continual development of the synthetic rubber manufacturing industry, marked improvements in the compounding of natural rubber will result in better vulcanisates for pharmaceutical purposes. The synthetic rubbers will be of increasing interest particularly as better methods of stabilisation, rendering the use of objectional chemical additives unnecessary, become available and as increasing exprience is gained in compounding the new rubbers.

The improvement of rubber compounds for use in pharmacy is not, however, a one-sided affair solely concerning the rubber manufacturer,

there is a constant need for the pharmacist to play his part in continually pointing out the problems and difficulties raised as developments in his field proceed.

As Raven has pointed out in his recent Gifford Lectures[18], the relative stagnation of medieval industry was due in some measure to the hierarchial orderings of the separate callings and professions which repelled all attempts to pass discoveries in one field to others and so contribute to the solution of problems in other fields.   In a similar way, the problems raised by the application of rubbers in pharmacy are the joint concern of both rubber technicians and pharmacists and it is only by working together, each contributing his special knowledge, that real progress can be made.

References

1. Pickles, *Trans. Rubber Ind.*, 1951, **27**, 148.
2. Treolar, *Trans. Farad. Soc.*, 1940, **36**, 538.
3. Gee, *Trans. Rubber Ind.*, 1943, **18**, 266.
4. Boggs and Blake, *Industr. Engng Chem.*, 1926, **18**, 224.
5. Jones, *Trans. Rubber Ind.*, 1947, **23**, 46.
6. Pande and Ramakrishnan, *ibid.*, 1947, **22**, 325.
7. van Amerongen, *J. Appl. Phys.*, 1947, **17**, 972.
8. Shu Kambara and Kamakazu Ohkita, *Rubber Chem. Tech.*, 1952, **25**, 209.
9. Habgood, *The Designing of Technical Rubber Compounds, The Fundamentals of Rubber Technology—Eight Lectures*, Imperial Chemical Industries Ltd., 1947.
10. Webster, *R.A.B.R.M. Res. Rept.*, 12, Croydon, 1923.
11. Winkelman and Croackman, *Industr. Engng Chem.*, 1930, **22**, 1367.
12. Skinner and Drakeley, *Trans. Rubber Ind.*, 1932, **8**, 117.
13. Haworth and Pryer, *ibid.*, 1949, **25**, 265.
14. Hicks and Drakeley, *ibid.*, 1943, **18**, 231.
15. *Rubber in Engineering—Ministry of Supply, Admiralty, Ministry of Aircraft Production*, London, 1945, ch. 9.
16. Haworth, *Alchemist*, 1953, **17**, 274, 361.
17. Brazier, *Trans. Rubber Ind.*, 1938, **14**, 206.
18. Raven, *Science and Religion*, Cambridge University Press, 1953, pp. 91, 100.