A TYPICAL RUBBER TREE.

FROM THEORY TO PRACTICE
IN
RUBBER FABRICATION.

By

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Contents.

Preface.

This book is mainly the outcome of numerous enquiries that I have received, and am still receiving, from time to time from various sources:—"Please let me know the method of making balloons from latex";—"Please be so good as to state the method of manufacturing combs and fountain pens from rubber", still another—"I wish to start a rubber factory; will you please furnish me with the necessary documentation?" etc. etc. The three parts of this book reply to these and other similar queries.

The process of the manufacture of rubber goods of the past in general differs little, if at all, from that adopted at the present time, except perhaps in the case of a few items like tyres and tubes, the fabrication of which has been completely modified. This, however, does not apply in the case of formulas of rubber mixes for producing rubber goods. In early days rubber was not as cheap a thing as it is now, not to speak of the period during the Great War when the price of rubber in the German occupied countries such as Belgium, rose to the exorbitant figure of about Rs. 250/- per kilogram. Then to reduce the price of the rubber mix, the rubber manufacturer was obliged to incorporate in his formulas quantities of Kaolin or Whiting or Sulphate of Barium whithout paying any regard to the question of whether the use of one chemical was preferable to that of another or would help vulcanisation (which in those days lasted for two hours or more) more than any other chemical. In fact in those early days formulas were based on empirical principles, whereas now-a-days, due to the invention of accelerators, the technique of composing formulas for rubber mixes is more complicated, as one has to bear in mind that, whilst some chemicals activate the cure of the rubber goods, others have a retarding effect upon it. The vulcanisation of rubber goods is now a very delicate operation as it does not extend over a period of two hours as in the past, but is accomplished sometimes in two to four minutes. Examples of as many mixes as possible are given in this book which it is hoped will prove to be of considerable help to the Rubber Technologist.

A part of this book is devoted to latex and manufacture of goods from latex. When speaking of latex, one is inclined to call it a "new industry". This, however, is not correct since the use of latex is older than the manipulation of coagulated rubber in the manufacture of rubber goods. As an illustration, it will suffice if we remember Christopher Colombus finding people in America using rubber goods made from latex, when he landed there for the first time. Surely these goods were not made from vulcanised rubber, but from coagulated latex. In fact we follow this method when we produce what is called Crepe Soles.

The main difference between the early days and the present time lies in the method of preparing latex for making rubber goods, and in this respect it is certain that new methods have replaced the old method of working latex. In the third part of this book are various formulas for working the latex, and descriptions of the several ways of making rubber goods by the employment of these formulas are also given.

I owe a debt of gratitude to all those who have helped me directly or indirectly in the compilation of this book. By "those" I mean T. G. Crane Esq. of the Monsanto Chemical Works, The Farben Industry Laboratories, The Imperial Chemical Industries, and several others. My thanks are also due to the Rev. G. A. N. Shackle who has helped me from time to time with his valuable suggestions and advice.

JOHN HELEN.

FROM THEORY TO PRACTICE
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CHAPTER I.

The Raw Rubber.

AS an introduction to the treatise FROM THEORY TO PRACTICE IN RUBBER FABRICATION, let it be said that Rubber is extracted from a sort of milk—Latex—which is found in some peculiar trees, of which the Hevea Brasiliensis is the most valuable, as it produces the *Para Rubber* of prime quality.

There are several other kinds of rubber trees growing in Africa, in the Malay States, in the East Indies, and in certain parts of America, all these natural plantations being situated in the Tropical Zone.

Latex appears not only in the stem of trees, but is also found in some vines and shrubs as well.

It is said that Christopher Colombus, who discovered the New World, discovered the rubber tree also! While he was in Hayti, he beheld there people playing with balls made of a peculiar substance which was extracted from some of the trees growing there in abundance.

It was many years later that Priestly found out, by rubbing spots on paper with that peculiar substance, in the coagulated form, that he could make the spots disappear, and on account of this property, the substance has from that time been known as *Rubber*.

Progressively, but with timidity, other trials were made till the early years of the 19th century, when the rubber industry became an established fact.

A special climate is required for the cultivation of rubber trees, which develop themselves remarkably in moist soils with a temperature of from 85° to 90° F.

Unfortunately, irrational cutting of the rubber trees soon showed its disastrous consequences, and vast forests were doomed to premature annihilation.

To compensate for the destruction of these precious trees, trials were made to grow some of these plants in the tropical possessions of the British Empire, principally in Ceylon, where the cultivation of rubber made rapid progress.

In India, however, cultivation of the *Hevea plant* is of still later origin. Nevertheless, it may be stated that in the course of 50 years rubber plantations developed here in an unexpected manner.

Now-a-days, Travancore State, with its multiple plantations, all situated at an altitude of below 1000 ft., in the vicinity of the Western Ghats, in the Shencottah, Mundakayam and Rani Valley districts, has become the chief centre of Indian rubber production, comprising 80 per cent of the Indian crop.

150 trees are usually planted per acre, but after a few years they are thinned out to 140 per acre, the reason being that more trees per acre will retard the growth of the trees.

As already stated, the best rubber is obtained from the *Hevea Brasiliensis*, and it has been cultivated to the exclusion of other varieties in India. Rubber obtained from this variety is much stronger and possesses a much higher breaking strain than that of any other.

The trees are generally tapped according to what is known as the *Alternate Daily System*. By this method the tapping of the tree is done over half the area on an estate one day, and the other half on the following day. For tapping, the circumference of the tree is divided into halves, and only one half is tapped, up to 6 ft. from its base. A V-shaped cut on the perpendicular central channel is made with incision into the bark, at the bottom of which a half coconut shell is placed to collect the latex which flows along the cut.

When the bark has been removed over a wide area, the tree is allowed to rest for about four years. Great care is to be taken not to touch the cambium of the tree, as this not only injures the plant, but may also kill it.

The tapping is carried out in the early hours of the morning, as it is well known that the latex then leaves the roots of the tree, climbs spirally into the stem, and reaches the top at midday, from where it again flows down to the roots, so that by the evening there is no more latex in the stem, the richest latex being that collected at day-break.

Latex appears in the form of a milky fluid, the globule of rubber being suspended in drops, which contain from 60 to 80 per cent of water. The separation of the rubber from the fluid is carried out by straining the latex and then coagulating the rubber globules into a solid mass.

The latex generally coagulates itself, when it is allowed to remain for a certain time. It is then exposed to air for a given time, when the water escapes by evaporation and the rubber substance remains. This agglutination may be hastened by adding to the latex salt water, alum, or acid, but this process does not ameliorate the quality of the rubber, as the latter will become hygroscopic, the product becoming moist and sticky.

Other methods of coagulation are also adopted, of which the *Smoking Process* is the best known, and is applied in the Amazon district for the production of what is still called *Fine Para.*

Solid rubber melts at 248°F. into a viscid mass, which does not again harden when cooled down. It is unaltered by chlorine, hydrochloric acid, sulphurous acid, flurocilicilic acid, ammonia, or caustic alkaline lyes. Nitric acid and sulphuric acid act on rubber only when they are concentrated.

Vulcanised rubber swells up when mixed with solvents like naphta, benzol, benzine, carbon bisulphide, carbon tetrachloride, chloroform, ether, benzaldehyde, turpentine and the like, and forms a colloid solution, the rubber having a sponge or foam-like structure, so that the solvents, diffusing in by osmose between the walls, distend the rubber texture into what is called a rubber solution.

In early days—even in 1902, when the author joined, as an apprentice, the then only existing Cable and Rubber manufacturing company in Brussels—raw rubber came to the market in the form of lumps, balls, strips, hams and scraps, instead of clean sheets as at present. These generally contained a lot of sand, pieces of wood, hard nuts, and even stones, purposely hidden by the natives, by mixing them with the coagulated rubber, in order to make up the weight of the specified quantity of rubber, which they were to bring every day to the collector of their respective districts, with the result that when this rubber ultimately reached the rubber factory, the gear wheels of the Washing Mills often broke into pieces!

On an average, the weight of these stones and other impurities was not less than 10% of the weight of raw rubber. To this must be added a certain percentage of moisture, which subject will be dealt with separately in the following pages. All this foreign matter had to be removed from the rubber before it could be used by the manufacturer, and the first process in a rubber factory was to get the raw rubber washed in the washing room, where such heavy machines as *Hollanders* and *Washing Rollers* were provided. The rubber in small pieces was introduced first into the *Hollander*, where the main impurities were separated.

The *Hollander* is an oval tank made of iron, about 6′ wide and 15′ to 18′ long, with a beating pulley running in it. When filled with water, the rubber pieces, being beaten by the beating pulley, run round and round, but never get crushed. After some time, the bark, which is lighter than water, floats on the surface and is skimmed off, while the sand settles down on the bottom of the tank.

After this first operation, the rubber is removed from the *Hollander* and washed in the heavy duty *Washing Rollers*, from where it comes out in the form of long sheets, which are allowed to dry in a well aerated and well heated room. The sheets remain in this state for several days, if not for weeks.

This was the way in which, in olden days, raw rubber was washed and cleaned by the manufacturer. Since then, the plantations have been supplying the rubber in crepe or smoked sheets, ready for use in the rubber factory, and there is no need for us to consider further that washing process, which now belongs mainly to the past.

As an indication, however, the following is the nomenclature of the various qualities of rubber, with their percentage of moisture, which came to the market in those days. The *Hevea* sorts from the Amazon districts, such as:

Para Fine and Para Negro heads contain from 15 to 20% moisture.

The Mangabeira of American origin	contain from	15	to 30%	moisture.
The Cameta of American origin	contain from	40	50%	,,
The Cernamby Manaos of American origin	contain from	20	35%	,,
The Peruvian Scraps of American origin	contain from	18	22%	,,
The Flakes of African origin	contain ,,	25	35%	,,
The Thimbles of African origin	contain ,,	18	35%	,,
The Gambie of African origin	contain ,,	20	30%	,,
The Conakry of African origin	contain ,,	30	35%	,,
The Leona Nigger of African origin	contain ,,	30	35%	,,
The Lumps of African origin	contain ,,	30	40%	,,
The Niggers of African origin	contain ,,	18	35%	,,
The Cameroun Balls of African origin	contain ,,	18	25%	,,
The Upper Congo Red Balls of African origin	contain ,,	20	25%	,,
The Upper Congo Lopori of African origin	contain ,,	18	24%	,,
The Kassai Black Twist of African origin	contain ,,	20	28%	,,
The Kassai Red Twist of African origin	contain ,,	22	28%	,,
The Kassai Ball Twist of African origin	contain ,,	20	26%	,,
The Mozambic of African origin	contain ,,	12	36%	,,

The Madagascar of African
origin contain from 28 to 36% moisture.
The Assam of Indian origin
contain „ 12 45% „
The Penang of Asiatic origin
contain „ 12 18% „
The Borneo (Pontianac) of
Asiatic origin contain „ 50 75% „

A special mention should be made of the *Guayule*, of which much has been said in the past by American reviews, for the reason that it is an American product. The Guayule is not appearing as latex like the other sorts, but, just as in the case of *Gutta*, in shrubs, vines, roots and leaves, which are crushed in water, on the surface of which the light bark and the rubber floats, the heavy wood going down the water. By repeated washings, the mass containing the rubber is driven from one tank to another, and finally the Guayule is collected, well cleaned by the washing process, reduced into sheets and dried, after which it is ready for use in the rubber factory.

It is well-known that rubber contains *Resin*, and Resin is a destructive agent to rubber goods. It is therefore imperative that it should as far as possible be separated from the rubber molecule. Unfortunately, the total extraction of the resin is impossible, with the result that little particles, which remain, develop themselves, when the manufactured rubber is ageing. As a matter of fact, it may be stated that all qualities of rubber do not contain resin in the same proportion. For instance, the hevea rubber—the para—which is the rubber of prime quality, contains only from 1½ to 3% of resin, whereas the prime Assam of lower quality from 14 to 16%, the Upper Congo 14%, the Brazillian Strips 28%, the Mexican Guayule 25% and the Pontianac 75%.

There are various ways of extracting the resin from the rubber, and various apparatus have been constructed for this purpose: the *Chute Deresinating Apparatus*, the *Eves Process*, the *Lawrence Deresinator*, the *Flament Process*, the *Haddan Resin Extractor*, the *De la Fresnaye Deresinator*. A few are of French origin, but many more of British and American origin.

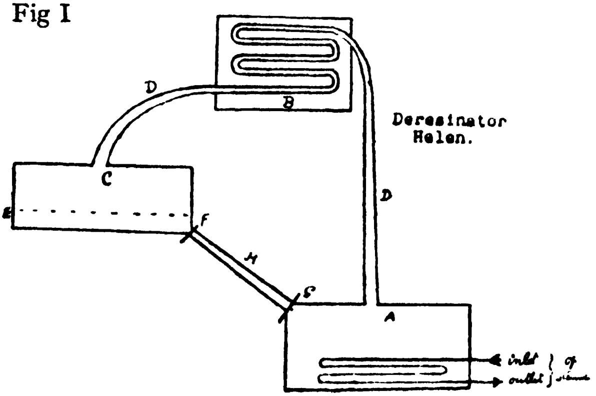
By most of the above apparatus, the rubber is either dissolved in naphta, and the resin precipitated by some addition of alcohol, the rubber remaining as a solution, or the rubber is dissolved in naphta and precipitated by addition of acetone, and in this case it is the resin which subsists as a solution.

But all these processes are costly due to the use of solvents like naphta and acetone. That is why we agree with Dr. Weber, who declares that the best method of extracting resin from the rubber is the *Soxhlet Method*, using methyl alcohol as a dissolvent of the resin, the rubber not being dissolved at all.

The following Deresinator (Fig. 1) was constructed by the author and was in use in a Belgian factory which he managed a few years ago.

The process of the working of this apparatus is described hereafter.

Fig I



The rubber well washed and reduced in fine sheets is introduced, after being completely dried, into tank C. The methyl alcohol stored in the tank A is heated by steam and alcoholic vapours will escape through the conduit D, which passes partly in the serpentine through the tank B, filled with cold water, so as to have the alcoholic vapours condensed, which falls by drops on the rubber sheets in tank C, lying on a sieve made of aluminium. When the rubber in tank C is completely immersed in alcohol, the alcohol is allowed to remain there for 6 to 12 hours during which time a part of the resin dissolves.

Then, opening the tap F, the alcohol with the dissolved resin returns through the draining pipe H to tank A, where the same operation starts again till the rubber contains as small a proportion of resin as possible. To ascertain the quantity of resin extracted by the methyl alcohol, a sample, taken from the rubber in tank C after each immersion, is mixed with the required quantity of sulphur and vulcanised, to be analysed by the following method:

Method of Analysing Rubber as adopted by the Belgian Railway Laboratories. Rasp with a coarse file 2 to 3 grams of the vulcanised rubber sample taken from tank C of the Deresinator Helen and introduce it into a glass balloon of 300 cc. capacity, containing 50 cc. of an alcoholic solution of caustic soda at 5%. Boil it for four hours, the balloon immersed in a receptacle containing boiling water and surmounted by a refrigerator. Then separate the liquid by washing the vulcanised rubber again and again with boiling alcohol of 96° strength. Add distilled water, which must evaporate until the smell of alcohol has completely disappeared, the quantity of water to be added being not less than half a litre. Add to this solution 25 cc. of a concentrated chlorhydric acid to free the greasy acids of the produced soaps. Extract these with ether and recuperate the etherous liquid in a tared crystalliser. Then evaporate the ether and take the weight of the greasy acid, which is the weight of the resin still present in the rubber immersed in tank C.

CHAPTER II.

The Vulcanisation of Rubber.

CHARLES GOODYEAR made, in 1842, a notable discovery, when he found out the peculiar action of sulphur on rubber. On realising that raw rubber could never be of much use in its natural state, and after many trials, he immersed a sheet of rubber in melted sulphur, and realised that, while a part of the sulphur was absorbed by the rubber, the latter underwent important changes in many of its fundamental characteristics: the rubber was no longer affected by changes of temperature, was no longer porous, lost its solubility in the solvents, was no longer plastic, but became elastic—permanently elastic.

Later on, other experiments were made, during which the sulphur was incorporated into the rubber by means of masticator, or better still, by powerful mixing rollers, and the result was identical as in the case of immersion of rubber in a bath of melted sulphur. Since, the curing of rubber has been called *Vulcanisation.*

The question then arose as to the quantity of sulphur to be added and the degree of temperature at which it was to be heated to get the rubber properly vulcanised. After several trials, it was found out that 8 parts of sulphur to 100 parts of the raw rubber was the right proportion for having a vulcanisate of durable resistance, provided the cure lasted for not less than 2 hours at 280° Farenheit, taking into consideration the thickness of the rubber which was to be vulcanised. So this process went on in factories, and patents were taken. Rubber was vulcanised either in moulds or wrapped in fabrics, or vulcanised in talcum, the latter process being called *the cure in open steam*, and industry, which was adopting the rubber in its multiple varieties, was benefitting day by day by the use of the new product. The question now arises whether, if Charles Goodyear, the American, had not found out the principle of vulcanising rubber, industry would have adapted itself to the use of this famous product? It can at least be affirmed that these vehicles running 50 miles an hour, called motor cars, would never have seen the light of day, if they had been deprived of wheels with rubber cushions, called tyres!

Later on still, in the course of time and experience, others discovered that the rubber could be vulcanised by *cold process* as well. They dipped the rubber article into a solution of sulphur chloride with a solvent such as carbon bisulphide, and by an immersion lasting a few seconds, the sulphur chloride with the aid of the solvent, penetrated the rubber, and the vulcanisation took place under the combined effect of sulphur and the chloride. This method is generally called the *Liquor Cure*, whereas the method by which rubber is vulcanised with the vapour of the chloride of sulphur is called the *Vapour Cure.*

The solvent should be an agent which assimilates easily with the sulphur chloride without decomposing the product, and must be able to swell the molecule of the rubber. The best solvent known is Carbon Disulphide which is highly inflamable, volatile and poisonous. The percentage of sulphur chloride must be low and never exceed 3 %. If there is an excess of sulphur chloride, the vulcanised rubber should be washed in a solution of water with soda, the latter decomposing the residue of sulphur chloride and neutralising the hydrochlorite acid, which was formed by the reaction.

Whiting, Magnesium and Litharge, which are chemicals of basic character, should never be introduced in mixes which are to be cold vulcanised, as these minerals react on the sulphur chloride by decomposing the chemical. The sulphur chloride is of amber colour, fumes in the open air and produces vapours affecting the eyes and nose.

As water decomposes sulphur chloride, the latter should be protected against humidity.

The sulphur chloride is also dissolved in carbon tetrachloride and in dichlorithylene, of which the specific gravity is 1.265 at the boiling point 48° C., and these solvents are *non inflamable.*

Seamless articles, such as balloons, teats and the like, are generally cold vulcanised. We will see in the chapter devoted to Latex that there are other means of vulcanising these seamless rubber goods.

Cold vulcanisation is also used for the curing of rubberised fabrics for raincoats, hospital sheetings and groundsheets. The rubberised fabric passes over a polished wooden roller immersed in a bath of sulphur chloride and carbon bisulphide, or any other solvent as the case may be, the solution being contained in a wooden receptacle, lead-lined, as the chloride of sulphur does not attack lead. Simple contact with the solution suffices to get the rubber-coated fabric fairly vulcanised, after which the rubberised face is powdered with starch, potato flour, or licopode powder.

Scientists are of the opinion that the cold cure should only be used in temperate climates, and not in the tropics. The author does not agree with this assumption, because, while in Europe, where he was using a solution of 3% of sulphur chloride dissolved in carbon bisulphide, which was giving satisfactory results, he obtained in India—in Karachi as well as in the

South—the same satisfactory results, by using 1½% of sulphur chloride in the solvent, with the result that the rubberised fabrics, like the joints on bicycle tubes so vulcanised, were still, after six years, as good as could be expected. No doubt, so far as ageing resistance is concerned, hot cured articles are superior to those cold vulcanised, but the ageing properties of cold cured rubber can be improved, and it is suggested that the peculiar *Nonox CC* from the Imperial Chemical Industries, designed to retard the ageing of cold vulcanised rubber is the suitable antioxidant for this purpose, and Nonox CC should be incorporated in the rubber mix at the same time and in the same way as the other ingredients, in the proportion of 1½ % on the weight of the crude rubber. As Nonox CC, however, is not entirely free from staining, it should not be used in the case of very lightly coloured rubber mixes.

The Imperial Chemical Industries conclude that the antioxidant power of Nonox CC may be gauged from the fact that a sheet of rubber, containing 1½ % of Nonox CC on the rubber content, cold cured in sulphur chloride and then sweetened in ammonia gas, was still eminently serviceable after two days ageing in the oxygen bomb, whereas a sheet made from the same mix, but without Nonox CC, completely perished after the same treatment.

Hot vulcanisation was adopted all over the world. Manufacturers of rubber goods were perhaps finding that a 2-hour cure was not only costly, but handicapped their means of production. So they tried, in their respective spheres, to find some means of reducing the 2-hour vulcanising time, and they finally found out that by combining sulphur with litharge, or lime, or carbonate of magnesium, or minium of lead, the vulcanisation of rubber could be obtained at a lower temperature, round about 270° F., with a reduction in time, say of half an hour at the most, but that was all they knew in olden days about accelerating the vulcanisation.

It was when the real Accelerators made their appearance that the Rubber Industry was filled with amazement, the new accelerators being not only able to reduce the time of vulcanisation, from two hours to 3 or 5 minutes, but, as mighty agents, they were also capable of ameliorating the physical properties of the rubber as well. A few grams of an accelerator, combined with sulphur, in a rubber compound of about 20 lbs. in weight, could produce such a miracle!

CHAPTER III.

Antioxidants.

BEFORE discussing the various accelerators now in use, it is desirable to say a few words about the Antioxidants, the names of which are already too numerous; for instance:

Aldolalnaphthylamine,
Phenylanaphthylamine,
Phenylbetanaphthylamine,
Diphenylamine,
Oxynone,
Resistox,
Nonox CC,
Flectols,
etc. etc. etc.

As the author has worked specially with those produced by Monsanto, he intends to discuss the Flectol types, which constitute the latest developments resulting from rubber compound researches.

What are Antioxidants? They are a class of compounds which are added to the rubber stocks in order to delay the perishing of that stock until a considerably longer period has elapsed than would normally be the case. It must not be imagined that the use of antioxidants is a general remedy for the many difficulties with which rubber compounders are faced. Antioxidants are added for one purpose only, namely to slow down the rate of perishing or oxidation of the rubber. In practically all classes of goods, where prevention or deterioration of this type is demanded, a good antioxidant must be added and for this purpose, after trials, the Flectols were adopted.

Flectol B is a thick, dark coloured, treacle-like liquid which is sufficiently thin at all normal room temperatures, so that it may be poured from the container without difficulty. It mixes readily into any rubber batch on the mixing mill.

Flectol H is a powdered resinous material, light in colour, with a melting point somewhat above 100° C.

Chemically, Flectol B and Flectol H are of the same category, and are produced from the same basic materials. Their effective antioxidant properties are very much the same. Flectol B, being a somewhat thick liquid, gives some softening effect during the mixing operation, and many prefer this material for this reason, whilst others prefer the powdered Flectol H, which is, no doubt, easier to handle in the compounding room.

As previously mentioned, Antioxidants should be used for the primary purpose of delaying oxidation or perishing of the rubber article into which they have been incorporated. They have certain secondary benefits that seemingly are additional properties, but further thought on the subject makes one appreciate that these additional benefits are only different ways of expressing antioxidant values.

The *American Agerite White* for example is a so called non-staining antioxidant, but a smaller percentage of the Monsanto Flectol H will give the same non-staining properties with still better oxidation resistance. For instance, if one is using 1% of Agerite White, one can use ¼% of Flectol H, obtaining still a better oxidation resistance. If found necessary, the Flectol H can still be increased up to ½% or 0.75% without causing too great a discoloration of the finished product.

Anti-oxidants being amines, or substituted amines, they cause discoloration, not only of the rubber goods, but of the paper in which they are wrapped. With certain types of paper, the staining is accentuated, and may have a quite bright colour. This is due to a trace of reducing agent left in the paper from a bleaching process. No harm, however, is done to the rubber articles, although, naturally, a discoloured paper is not a very pleasant wrapping.

Flectol H, from the purely perishing point of view, is supreme in the protection that it provides, yet it combines with this property, that of resisting discoloration to a very marked degree.

There are many anti-oxidants which claim never to discolour a white stock—there are still many more which claim great resistance to oxidation. What is so difficult to find is an anti-oxidant which may be used in white or light coloured stocks and yet will also provide first-class resistance to oxidation. It has been found that Flectol H meets these dual requirements.

In fact it is becoming more and more generally recognised that there is no such thing as an absolutely non-discolouring effective anti-oxidant. Flectol H is no exception to this, in that given time, it will discolour, only stocks containing Flectol H will take considerably longer to discolour than those containing other so-called white anti-oxidants. Despite this, the same material may be used in tread stocks, tube stocks and everywhere where maximum heat and oxidation resistance is demanded, and the manufacturer using Flectol H, says Monsanto, may feel certain that there is no other equally effective anti-oxidant at present existing.

This is indeed a very broad and ambitious claim put forward by the Monsanto R. S. L., who explain further that Flectol H is a solid polymer, and that it has a melting point of about 100°C. Finely ground, it is a buff coloured powder, which readily mixes with the rubber, and there are no difficulties connected with the use of it, as Flectol H has no effect on the rate of cure, the softening action being negligible when used in the correct proportions of from ½ to 2% on the rubber content of the batch. It does, however, increase the flexing capabilities of a stock enormously—a property which is of paramount importance to the tyre compounder. Compared with Flectol B, essentially no difference can be detected, and it should be understood that the reasons for Flectol H being introduced are that the latter may be used in white stocks whilst Flectol B should not, and that Flectol H is a solid and is thus considerably easier to handle. Apart from these considerations, the two materials are strictly comparable.

In conclusion, Monsanto compares Flectol H with Phenylbetanaphthylamine in the following tread stock formula:—

Formula	**A**	**B**	**C**	**D**	**E**
Sheets	100	100	100	100	100
Zinc Oxide	8	8	8	8	8
Carbon Black	42	42	42	42	42
Tackol	3	3	3	3	3
Stearic Acid	4	4	4	4	4
Pine Tar	2	2	2	2	2
Sulphur	3	3	3	3	3
Thiotax	1.1	1.1	1.1	1.1	1.1
Phenylbetanaphthylamine	1.0	-	-	-	-
Flectol H	-	0.7	0.8	0.9	1.0

Cures were made for 30, 45, 60, 75, and 90 mins. at 25 lbs. (130°C).

Cure	Stock	Modulus at			Tensile	Ult.
		300%	500%	700%	@ Break	Elong.
30/25 S. 130	A	945	2220	-	3455	665
	B	895	2240	-	3320	645
	C	980	2275	-	3605	685
	D	928	2210	-	3555	690
	E	918	2215	-	3510	680
45/25 S. 130	A	1240	2815	-	4165	665
	B	1243	2870	-	4095	645
	C	1285	2830	-	4090	655
	D	1280	2830	-	4180	660
	E	1280	2830	-	4105	645
60/25 S. 130	A	1435	3085	-	4345	640
	B	1448	3215	-	4275	620
	C	1463	3130	-	4300	630
	D	1453	3145	-	4245	635
	E	1443	3180	-	4220	610
75/25 S. 130	A	1545	3245	-	4285	600
	B	1570	3395	-	4230	580
	C	1543	3400	-	4325	605
	D	1528	3330	-	4340	610
	E	1545	3395	-	4255	590
90/25 S. 130	A	1750	3650	-	4285	570
	B	1695	3610	-	4180	560
	C	1730	3565	-	4170	570
	D	1708	3600	-	4235	575
	E	1710	3605	-	4190	570

The 75 minute cure was selected as being a full cure and representing the average cure given tyres, including small and large sizes. This cure was aged for 89,120,144 and 168 hours with the following results:—

Oxygen Bomb 70°C - 300-lbs. pressure.

			300%	500%	Tensile	Elong.
75/25	S. 130	A	1495	2645	2700	525
	Aged	B	1535	2760	2760	500
	89	C	1585	2750	2795	510
	hours	D	1580	2780	2780	500
		E	1585	2930	2930	500
75/25	S. 130	A	1360	-	2320	485
	Aged	B	1345	-	2230	490
	120	C	1445	2510	2355	475
	hours	D	1495	2505	2525	505
		E	1465	2620	2605	495
75/25	S. 130	A	1350	-	2050	455
	Aged	B	1350	-	2140	475
	144	C	1395	-	2180	470
	hours	D	1420	-	2265	480
		E	1445	-	2335	475
75/25	S. 130	A	1215	-	1675	410
	Aged	B	1195	-	1570	410
	168	C	1230	-	1690	415
	hours	D	1290	-	1740	430
		E	1325	-	1860	435

From the above figures it can be noted that Flectol H has no effect on the rate of cure.

The E stock containing 1% Flectol H has the best ageing properties; considerably better than the A stock containing an equal amount of Phenylbetanaphthylamine, and .75 of Flectol H gives equal ageing to 1.0 of Phenylbetanaphthylamine, the latter being on the market under various trade names as Neozone-D, Age-rite powder, Stabilator AR, Antioxidant MC, and the like.

CHAPTER IV.

Softeners.

THE Monsanto Softeners are the Cycline Oil, the Tackol, and the A-510.

Cycline is a trade name given to the particular blend of oils designed by the research division of the Rubber Service Laboratories Co. for use in rubber compounding. It is a neutral oil for softening the stocks sufficiently, without overmilling, to provide for easy smooth calender and tubing machine operations.

It is well known that other substitutes such as Naphthalene, Naphthalene oils, Rosin, Turpentine Oils, and the like, when heated with rubber cause rapid depolymerisation, or disaggregation, of the rubber molecule. It is also well known that oils such as castor and other vegetable oils cause a very mild depolymerising effect, when incorporated into rubber and heated. Other vegetable and mineral oils and distillates of coniferous origin are classified between these extremes. The oils in Cycline are blended in such proportions as to give sufficient disaggregation to provide suitable working properties during factory processing, but not enough to induce rapid oxidation and deterioration of the molecule.

Stocks containing varying amounts of Cycline have been aged, both artificially and naturally, and the ageing properties of the softener have been found equal to any, and indeed superior to most of the commonly used somewhat similar material on the market now-a-days.

In general, most of the naval store products, when incorporated into rubber, add materially to the tack of the resulting mixture. Frequently, one desires to increase the softness or plasticity of a mix without materially increasing this tack. It is here that Cycline should be used. For mixes in which additional tack is desired, Tackol should be incorporated.

Cycline is usually used in proportions ranging from 1 to 5 per cent on the rubber content. Where very soft stocks are desired, as high as 8 to 12 per cent may be used. As the quantity is increased, one should watch its cure, for, as stocks become softer, they require a correspondingly greater amount of sulphur to give a good technical cure.

Very high reclaim content stocks are usually quite sticky during milling, and adhere very tenaciously to the mill rolls, particularly if milled hot. The same stocks are, however, quite dry and have little tack when cold. The addition from 2 to 4 per cent of Cycline Oil to these stocks will make them mill very easily and permit the stock to come off the mill rolls freely. Considerable quantities are regularly used for this purpose.

Cycline is therefore generally used in stocks, normally sufficiently tacky in themselves, in which increased plasticity is required.

Tackol. The manufacture of articles from a compound containing essentially reclaimed rubber is somewhat difficult, particularly, if the article must be built up of different pieces of stock. The stocks themselves quickly become dry on the surface after milling, and do not adhere to each other properly. High carbon black tread stocks also quickly become dry on the surface, and it is frequently difficult to make such a tread stock adhere firmly to adjacent stocks.

Various materials have been added to rubber compounds to overcome these conditions. Of all the types of materials that have been used, the Pine products have been the most successful. Unfortunately, the naval store products are produced in a widely diversified manner, and it is exceedingly difficult to duplicate one's results. Certain of the Pine products are quite unsatisfactory from the standpoint of permitting good ageing of the rubber products in which they may be used.

The Rubber Service Laboratories Co. state that they have long since realised the fact that the rubber industry would appreciate a material which would always be uniform and which would keep the type of stocks mentioned in a tacky condition. After considerable research on the subject, they say that a certain blend of several resins and oils was found which would accomplish the desired results. A longer time was necessary for them to standardise these materials, so that the uniform product could be manufactured. They affirm that this was accomplished several years ago, and Tackol has since been offered to the rubber manufacturers as a standardised material for producing tack in rubber stocks.

Tackol holds back the bloom in uncured stocks to a remarkable degree. It gives quicker milling and permits of cooler stock on the mill. It also allows better distribution of pigments in the batch. It likewise facilitates the production of smooth extruded stocks.

Tackol is particularly suitable for keeping high reclaim content stocks and tyre tread stocks from drying out.

It is used in quantities of from 1 to 5 per cent on the batch weight.

The addition of Tackol to a stock will provide the type of tackiness which allows it to stick to itself, but which comes free from the mill or calender roll quite readily. While Pine Tar and Pine products will provide tackiness in a high reclaim mix, their use usually makes the stock stick badly to mill rolls, particularly if the batch is soft and the rolls quite hot.

The use of Tackol is now almost universal, as it is an all-purpose softener for the ordinary run of compounding. It is suitable for light coloured stocks as well as direct ones. It works well in all compounded and high reclaim stocks, and furthermore, it is uniform in its softening properties from day to day.

One most important use of Tackol is in the making of a rubber gas black master-batch, particularly in enclosed mixers. Here 50 parts of rubber, 50 parts of the black and 2 parts of Tackol give very rapid mixing and an excellent dispersion of the black.

Tackol, while viscous and sticky, is sufficiently liquid at all normal temperatures to be run directly without preheating from the steel shipping drum to the compound room container. All ingredients in Tackol are especially selected for the purpose, and each as well as the resultant mixture, will show very satisfactory ageing quality.

A-510 is the Rubber Service Laboratories Co.'s trade name for a type of soft formaldehyde aniline. Chemically, it is neither methylene-dianiline or formaldehyde aniline, but a product in composition between these two.

A-510 is a soft light yellow, almost white amorphous material, which readily melts down on the mixing mill and is quickly absorbed by the rubber. It has an exceptionally pronounced softening action during the processing operations and permits the rubber to be calendered or extruded very smoothly. It does not cause sticking to the calender rolls, but at the same time gives decided softness to the stock. This softness disappears during vulcanisation, and the finished product retains the full desired rigidity. This should be particularly noted, because the addition of all ordinary softeners, while facilitating factory operations, gives products which are not correspondingly soft after vulcanisation and which ordinarily make the rubber considerably more susceptible to oxidation.

At high calender temperatures, the formaldehyde odour of this product will be quite pronounced, and in large rooms, good ventilation or hoods over the mills and calenders must be installed in order to ensure the workers' comfort. On cool mills, calenders, or exturding machines, the odour is not noticed.

The various formaldehyde products were formerly used as mild accelerators, but in recent years, since the development of more powerful accelerators, the use of formaldehyde products is largely restricted to compounds where their peculiar softening action during processing is required. They are sometimes used further to act as secondary accelerators.

A-510 is usually used in quantities from 3/8 to 3/4 lbs. per 100 lbs. batch. It is particularly useful in handling tread, solid tyre, or other tough stocks, and about ½ per cent is customarily used here.

A-510 can be used in all types of stocks, except pure white ones, where a slightly yellowish discoloration appears on ageing. With ordinary light shades, it is, however, quite satisfactory.

Another softener is the German *Rubberine-Gel*, which was pushed in the last few years rather widely all over the Continent. In fact, much advantage has not been achieved in using it in the ordinary rubber mixings. A sample of this product has been analysed in the laboratory, and it appears to be a mixture of factice together with some oil. The resultant effect is that it has a very marked softening on rubber, and at the same time absorbs a certain amount of the sulphur present in the mix. But it is not yet established that some of these very efficient softening agents for rubber are all that one could desire, as they tend to depolymerize the rubber rather too greatly for it to be readily built up again during the vulcanisation. Certainly, if one can do as the German maker says, namely, adding a small percentage of the Rubberine-Gel to the ground waste rubber and so obtaining a first-class reclaim, the German product should be worth its money. The question arises whether anybody has carried out the said operation, not in a laboratory, but on any large scale in the factory?

What is just said is a reflection of the author's opinion. Let us see what the maker says about his product, which he pretends to be a new specific class among the rubber ingredients.

There is no product, he says, with such manifold properties as Rubberine-Gel shows. All previous softeners were fatty or oily substances, therefore water-resisting. Their action was merely mechanical, where as Rubberine-Gel behaves as hydrophillic and lyophillic. During the process of vulcanisation, Rubberine-Gel, of course, loses the hydrophil and lyophil power which it shows in the unvulcanised mix, so that the finished vulcanisate does not retain these properties. It absorbs water and renders it harmless.

Rubberine-Gel also acts as an emulgator and despersing agent. A thoroughly stable emulsion may be made from 100 cc. water plus 1 gr. ammonium bi-carbonate and 10 gr. Rubberine-Gel, by well shaking this mix. It increases the wetting of fillers in rubber and diminishes surface tension.

Further factory tests with Rubberine-Gel have shown, says the maker, that about 5% of this product may be substituted for 10% stearic acid, if 5% zinc oxide plus 6% lead oxide become activated simultaneously. This accelerating activation does not only occur with lead oxide, but also with the accelerators of the Mercapto group. Such an effect had previously been deemed impossible. As even a small addition of only 0.4% Rubberine-Gel already has a noticeable effect as an accelerator, it might have been assumed that the addition of 5% of this product would lead to strong over-vulcanisation. It was therefore very surprising to observe that 5% of it did not cause over-vulcanisation, even with twice the normal time of vulcanisation. This new observation made it possible to use it in similar quantities as other softeners and to replace stearic acid by half the quantity of Rubberine-Gel.

Investigation into the rule of subtitution by half the quantity of Rubberine-Gel showed that the other half was water retained by the said product and well distributed, that strictly speaking, therefore, not dry Rubberine-Gel was the softener, but the mixture: Rubberine-Gel plus water. When water was lacking in the mixture, Rubberine-Gel acted badly; if water was then added, so that the proportions of Rubberine-Gel and water were equal, mixing became easier.

In view of this, the following method is suggested to be adopted: start the mixing by throwing "dry" rubber on the mixing rolls. This apparently "dry" rubber still contains about 1% water. If no time is allowed to elapse and about 1% Rubberine-Gel is added immediately, this mixes without much trouble with the still damp rubber. If now the necessary quantity of active carbon black is added, e. g. to 100 parts rubber plus 1 part Rubberine-Gel, the usual 50 parts carbon black, a further 1.5 parts water thereby go into the mixture, and another 1.5 parts Rubberine-Gel can thus be added without trouble.

There would then be present:

99	parts	Rubber
2.5	„	Rubberine-Gel
2.5	„	Water
48.5	„	Active Carbon Black
152.5	parts	Master-batch.

Whilst this master-batch is being masticated on the mixing roller, the water evaporates very easily on account of the heating by friction; it is therefore desirable to add fresh water during the mixing to replace the evaporating water.

Rubberine-Gel does not, however, merely serve for the preparation of carbon black master-batches, but is also chosen to react afterwards with lead oxide, zinc oxide etc. or to stimulate the action of Mercaptobenzothiazol. That is why, for example, 5 parts Rubberine-Gel are added to 100 parts rubber, and preferably also a little water, for Rubberine-Gel by itself may in some circumstances, render the mastication more difficult—if the water naturally present has already evaporated—, and there will be present:

99	parts	Rubber
5	„	Rubberine-Gel
5	„	Water
48.5	„	Active Carbon Black.
157.5	parts	Master-batch.

The preceding remarks show that Rubberine-Gel is a valuable ingredient to the Rubber Industry.

The maker declares that the addition of Rubberine-Gel facilitates the fine lamination of reclaimed rubber. It is added to the reclaimed material whilst the latter is still moist, because Rubberine-Gel itself, plus a little water, has a great softening effect.

If ground waste rubber of medium specific gravity (1.3—1.5) is digested with up to 10% mineral oil, it requires about 15—20 hours heating at 57 lbs. steam pressure, but even then it often remains granular and not sufficiently softened.

If, however, 90 lbs. ground waste rubber of medium specific gravity is heated with 9 lbs. spindle oil or any other light mineral oil plus 1 lb. Rubberine-Gel, for 10 hours at 57 lbs. steam pressure, a well softened and non-granular plasticated rubber waste is obtained and easily laminated.

If the product as per the following formula is cured for 15 minutes at 43 lbs. steam pressure, the vulcanisate is shown to be equal in every respect to a whole tyre alkali reclaim which has been vulcanised correspondingly.

Plasticated rubber waste	85.83 %
Arrow Carbon Black	9.44 %
Diphenylguanidine	0.43 %
Sulphur	4.30 %
	100.00 %

If the ground waste rubber to be plasticated contains much white substitute, 1 lb. Rubberine-Gel may first be emulsified with 1 lb. of strong caustic soda lye; this emulsion should be mixed with the mineral oil and added to the ground waste rubber. During heating, the substitute becomes saponified; the plasticated waste rubber needs only to be dried, preferably by lamination on hot rollers. As regards the acceleration of vulcanisation, a residue of 1% NaOH in the plasticated waste rubber is equal to the same NaOH residue in the common alkali reclaim.

In conclusion, the maker says that the following advantages are obtained by the use of Rubberine-Gel.

	Working Conditions.	Test Results.	Practical advantages.
MIXING	Shortens the time required for mixing up to 70%. Enables compounding of more and cheaper fillers. The mixes hold well to the rolls.	Facilitates compounding of fillers. Mixes are not slippery. (The rolls grip the mixes and do not slip.) More efficient than other softeners without their objectionable smell. Retains the *nerve* of the rubber.	Saves time. Saves power. Cheapens. Less odour.
CALENDERING AND SPEWING.	Easier calendering. Easier spewing.	Quicker calendering. Quicker spewing.	Saves time. Increases output.
VULCANISING	Acceleration of cure. Activation of inorganic accelerators, particularly litharge. Activation of organic accelerators.	Approximately equivalent to twice its weight of stearic acid. Activates inorganic accelerators.	Saving of material with less tendency to deterioration. Saves time.
PROPERTIES OF THE FINISHED PRODUCTS	Greater resistance to abrasion. Good flexibility. For sponge manufacture gives a greater volume of more uniform pores. For enamelled goods such as shoes gives better polish and prevents creases.	Greater tensile and elasticity. Good ageing; superior to all mixes without Rubberine-Gel. Better polish and no creases.	Lower production costs. Greater sales capacity.

CHAPTER V.

Accelerators.

IT is now proposed to develop the theory of those products capable of doing miracles, not only by reducing the time of vulcanisation from hours to a few minutes, but by modifying the physical properties of the rubber as well.

Before proceeding, let us consider whether the denomination *Accelerators* is the appropriate appellation for these wonderful products. Certainly they accelerate the time of vulcanisation, but this may also be achieved, to a certain extent, without the aid of accelerators, by elevating the temperature of cure. What is of paramount importance with regard to Accelerators is not this, but their power to modify the physical properties of rubber, and in our opinion the inventors of these products would have been well inspired if they had selected a more appropriate denomination.

However this may be, the discovery of organic accelerators has completely revolutionised the rubber industry, and no other discovery, apart from that of vulcanisation itself, has had such a profound effect upon the whole field of rubber technology.

> "The use of Accelerators" (repeating here what the Imperial Chemical Industries, London, write on this subject) "has resulted in such improvement in general wearing qualities of tyres, that it has been estimated that in ten years the 'saved wear' is equivalent to the wear resulting from the mileage of 2½ million cars running once round the Equator! and from the manufacturers' point of view, the saving effected by the use of organic accelerators has also been immense; they have enabled increased production to be effected, reduced the consumption of power and time of mixing by enabling increased amounts of softeners to be used, and in consequence

> increased quantities of reclaim to be incorporated into the compounds for any given purpose, with the result that a cheaper cost price could be attained".

In no time accelerators of all kinds and all names appeared on the market, and no rubber manufacturer was able to use them all. If he had tried, he would have found by experience that a good many accelerators of different denominations, and supplied by different makers, were of the same chemical composition.

So, the best way for the rubber maker is to adopt the use of certain accelerators, considering the climatical conditions of the country where the factory is located, bearing also in mind (1) that inorganic accelerators, such as lime for instance, are of basic nature, and capable of accelerating the rate of vulcanisation, whereas organic accelerators, such as those of the Amine group, have a retarding effect upon vulcanisation, (2) that simple Amines in their liquid form, although good softeners, are weak accelerators, and that their use in the factory is not possible on account of their toxic nature.

Scientists, in subsequent years, have discovered that by using some derivatives of these basics,—the aldehydes, for example,—the poisonous effect of the Amines could be rendered harmless, and in course of time, as a result of continual researches, one discovery paving the way for another, faster accelerators succeeded the simple ones, the important question of ageing property of the rubber compound never being overlooked.

As the various accelerators do not have uniformity of activity, the Imperial Chemical Industries suggest the use of Mercaptobenzothiazole, or Diphenylguanidine, which are of definite chemical substances, and of which the uniformity can easily be checked by a simple melting point determination test, in preference to the liquid aldehyde-amines, of which the chemical combinations are indefinite. Having studied a large amount of accelerators, as proposed by the makers, the author has worked them for years, and the results of his practical researches were definitely encouraging. The Monsanto Urekas and the Takars from Rhone-Poulenc were tried at the same time as the German Vulkazits, and while he was adopting progressively these products in his formulas, he tried also some of the American accelerators. From his continuous researches he realised that the following accelerators are of the same chemical composition:—

The Rhone-Poulenc	Diphenylguanidine, or the D. P. G., is the Vulkazit D from the German I. G.
” ”	Mercaptobenzothiazole, called the Rapid Accelerator 200, is the American Captax, is also the Thiotax from Monsanto and is the Vulkazit Mercapto from I. G.
” ”	Disulfure of Dibenzothiazyle, called the Rapid Accelerator 201 is the Vulkazit D. M. from I. G.
” ”	Disulfure of Tetramethylthiourame, called the Super Accelerator 501, is the Vulkazit Thiuram from I. G. and also the American Tuads.
” ”	Deferred action accelerators, called the Takars 1 and 2 are the I. G. Vulkazit F and the Rhodifax.
The American	Captax is chemically Mercaptobenzothiazole, and is identically the same as Thiotax.

The American	Altax is chemically the Disulphide of M. B. T. and is also chemically the same as Thiofide.
” ”	Butyl Zimate is only a trade name for a derivation of the Dimethyl Dithiocarbamic acid, of which the Ultra Zinc—D. M. C. is another derivate.

Finally, the Monsanto Urekas are the I. C. I. Vulcafor D. A.

The value of the Monsanto products is indisputable, and their reputation may perhaps be greater than that gained by the Vulkazits and the Takars.

The Monsanto Ureka is a trade name given to a rubber accelerator composed of mixtures of various Mercaptobenzothiazole esters and other ingredients. These different materials apparently re-act during the early stages of the cure to produce an accelerator of suitable activity. The original Ureka accelerator is described and claimed in United States, British and French patents. Ordinary Ureka is a light yellow powder with a specific gravity of 1.290 and a melting point of about 125° C.

It is generally admitted in the rubber industry that the lower the temperature of vulcanisation, which one is able to employ, the better the products that will be obtained. The trend, during the past few years, has been to a gradual reduction in this direction, and we have now approached a temperature somewhat limited by the ability of the machine in the factory to process the various stocks.

Then the hunt has been for the ideal accelerator that would permit the low temperature cure so highly desired, and still allow handling of the rubber stocks in the factory in the ordinary manner.

As soon as we speak of such an ideal accelerator, it is necessary to define what we consider an ideal accelerator.

Several years ago this was thought to be one that would give absolutely no cure until a definite temperature was reached, then quickly exert its full influence; and finally give no more acceleration even if the heating continued. This is proved to be far from the ideal. In the first place, no chemical has yet been found to function as an accelerator which would not function somewhat more slowly at a reduced temperature. It has also been found necessary for the accelerator to continue its activity, as the cure progresses in order to compensate for the heat disaggregation of the rubber. An accelerator that does not function in this manner causes a stock to grow softer on continued heating at the vulcanisation temperature, and the stock is said to revert under these conditions. Such a stock in service under somewhat elevated temperature is apt to soften seriously.

Unfortunately, a number of rubber chemists and other scientific men, who ought to know better, speak of a definite *Critical Temperature* for various accelerators, and assume that at a temperature below the one designated, these accelerators have little or no activity.

It may be said that there is no such thing as a *critical temperature* of vulcanisation for any accelerator. All accelerators will vulcanise at any reasonable temperature, if sufficient time is taken. Frequently one hears that such and such accelerator has a critical temperature of perhaps 100°C. One may find on experimental work that it will not vulcanise to a practical cure, or even to, what might be considered, scorching conditions, in 10 minutes at this temperature;

but if heated for 10 hours, one could probably obtain a very nice commercial state of vulcanisation. If one insists on stating a certain definite temperature and call it a *Critical Temperature*, then a time factor must also be introduced, and also a condition factor, stating under what conditions the compounds may be exposed to this temperature. It is as absurd to give a critical temperature of an accelerator, without defining these other conditions, as to name the price of any commodity without naming the quantity.

Monsanto defines that there are *Simple* as well as *Mixed* accelerators, and as the Urekas belong to the latter, apparently their activity depends upon the reaction between the two ingredients involved, inasmuch as neither ingredient alone is as active an accelerator as a mixture of the two. It occasionally happens that two different accelerators, when mixed, produce an effect entirely different from the normal addictive effect that would be expected by the use of two separate materials. In such a case, this increased acceleration is caused by the two materials being different in nature and being so constituted that during the vulcanisation, they will apparently re-act to form a more active accelerator. This effect has led a number of rubber compounders to try to mix any and all sorts of accelerators, hoping to strike upon some unusual combination that will be particularly effective. Ordinarily, of course, these mixtures give no unusual property. The art of rubber compounding went through the same series of stages, when the compounders of early days felt that it was necessary to add to a compound a small quantity of almost every known pigment. In latter years, the compounding of pigments has distinctly gone forward on a scientific basis. The same principle of using accelerators on a scientific basis is now rigidly adhered to by those familiar with their properties. In general, mixed accelerators merely confuse the issue, and unless there is some distinct scientific reason for using these materials, it is best to proceed with one.

Monsanto declare that they are unable to describe accurately the chemistry of the action of their Ureka accelerators. This is not surprising, when one considers the fact that as yet, no one has given a clear straightforward explanation of the action of any particular accelerator. All we do know is that the acceleration follows certain distinct lines, but why, we are unable to say. We can follow the course of the acceleration, noting its speed during the different stages of vulcanisation and comment upon that. This leads us to theorise on the primary action of Ureka. As just mentioned, this accelerator consists of two ingredients, neither of which in itself is a strong accelerator. As long as a stock containing this mixture is held at a low temperature, we have no active accelerator to speed up the vulcanisation. As we raise the temperature of the stock in order to start vulcanisation, we also possibly start the interaction between the two ingredients in Ureka. This would gradually build up the active material during the early stages of vulcanisation, and would account for the fact that there is a decided delay in the development of the activity of Ureka. We notice that for the first quarter of the cure, the stock seems to vulcanise very slowly. Near the end of this initial period, the acceleration gradually increases over a short period of time until a very rapidly accelerated stock is created. Finally, a vulcanisate having an unusually high tensile strength is obtained.

Normally, vulcanising temperatures are required to bring about this apparent change from inactive Ureka to build up an active accelerator, and the time necessary at any ordinary vulcanising temperature to bring about this re-action is about one-fourth of that required to reach the maximum tensile strength. This means that for the first portion of over-curing period, very little vulcanisation takes place. Hence, the stock remains soft, flows perfectly and moulds properly. This is a very important feature, as it provides great adhesion of the rubber to fabrics, when so used.

Since Ureka stocks remain relatively unvulcanised for the first quarter of their curing time, it follows that unless milled or worked at an unusually high temperature, stocks will not develop the active accelerator during processing. Ureka stocks are consequently unusually easy to handle in the factory, considering the activity finally developed during the vulcanisation. It is possible, of course, by milling Ureka stocks at a very high temperature to develop this accelerator, as referred to, and we then have the same difficulties in factory processing that one would have when using the ordinary fast accelerators. Hot milling, calendering, or hot storage could very easily cause the re-action referred to, and thus materially curtail the delayed action properties of Ureka.

The Urekas are normal low temperature accelerators. By this is meant that they normally operate at temperatures from 20 lbs. of steam (258° F) to 30 lbs. of steam (274° F). However, we know other conditions in the industry vary considerably, and Ureka may be used with excellent results outside of these temperatures, if used in the proper manner. We find naturally that the size and thickness of the article regulates the time of cure necessary. For average commercial articles in large bulk, such as motor car tyres and the like, the time of cure may be from 30 minutes to 4 or 5 hours, and the temparatures, referred to above, are suitable in such cases. Ureka is normally excellent for cures at the following times and temperatures:

3 to 15	minutes at	60	lbs. steam	(307° F)
5 to 30	„	50	„ „	(298° F)
10 to 60	„	40	„ „	(287° F)
25 Min. to 2	hrs. at	30	„ „	(274° F)
45 „ 4	„	20	„ „	(258° F)
90 „ 10	„	10	„ „	(239° F)

For all of these cures, the concentration of Ureka remains approximately the same. It is this concentration that gives the best results. An increase in concentration will permit of lower temperature cure, or of a slightly quicker cure, but a marked decrease in the concentration usually results in stocks having much poorer qualities.

From the above table it is observed that the use of Ureka is not recommended for long cures at temperatures above 270° F. In such a case one would use very small quantities of Ureka, and the full benefits of its use would not be obtained.

Ureka is classified as a non-toxic accelerator, and no trouble is experienced with this material, if it is handled in the usual way in the rubber factories. A reasonable degree of cleanliness must be prescribed, as with many other coal tar derivatives. The dry powder should not be permitted to remain on the hands, arms etc., particularly if the workman is perspiring. If this simple precaution is taken, no difficulties will arise. Once mixed into a rubber compound, the stock may be handled in any way whatever without trouble. At the time of writing, it has been used in quantity production for over five years, and many factories have used it in very large volume during this time without difficulties.

Ureka is a general purpose accelerator and may be used for press, open steam, and hot air cures. It is satisfactory for all types of stocks, with the exception of pure white ones.

Ureka may be used in light coloured stocks such as oranges, reds, yellows etc., but not in pure white, as it gives a yellow discoloration.

Generally, with Ureka, one uses from 2 to 3 parts of sulphur to 100 parts of rubber, and from 0.9 to 1.2 parts of Ureka to 100 parts of rubber. These ratios are for ordinary steam and press cures.

Ureka is likewise exceptionally suitable for hot air cures, such as footwear, proofing etc. Here one uses from 1.0 to 2.25 of sulphur and about 1.5 of Ureka to 100 parts of rubber. For all cures, one must use a small quantity of zinc oxide with Ureka, from 3 to 5 per cent of the ordinary zinc oxide or somewhat less of the extra fine quality being the usual requirements.

Litharge, Magnesium Oxide and Lime seem to have no necessary place in the compounding of Ureka stocks. Magnesium Carbonate may be used where a stiffening effect is required.

Carbon Black and Kaolin retard the cure of Ureka slightly and consequently a somewhat larger ratio of Ureka is used, when larger quantities of either of these materials are present in the compound. Both of these materials also increase the delayed action of Ureka and permit of very easy handling in the factory.

Acid softeners such as stearic acid, pine tar, wool grease etc., retard Ureka cures slightly, and likewise increase the delayed action somewhat.

Tensile Strength. Ureka gives stocks of unusually high tensile strength, approaching the results obtained by the true ultra accelerators. While tensile strength alone is not a direct criterion of quality, it is generally agreed that quality is ordinarily somewhat proportional to the tensile strength obtained.

Modulus. Ureka gives stocks of quite high modulus. This high modulus is generally desired for present day compounding inasmuch as this modulus, obtained by vulcanisation, may replace loading with fillers to a certain degree.

Hysteresis Loss. Ureka stocks are quite snappy, and when tests are made covering a work cycle, these stocks show up remarkably well in that the hysteresis loss is much smaller than with other common accelerators. This is true whether the work cycle be one of compression or one of tension. This fact means, of course, less heating in service for stocks which are operating under constant flexing conditions, such as pneumatic tyres, solid tyres, belting etc. Ureka is exceptionally adaptable for use in solid tyres, and large truck and bus pneumatic tyres, where this heating is ordinarily the greatest in practice.

Abrasive Value. Tread stocks and similar compounds cured with Ureka show abrasive results equal to, or better than, other materials now commonly used. There are a number of abrasive machines now being used for laboratory test purposes, and users are cautioned that some of these machines give erroneous results, when compounds are tested containing high percentage of waxes or wax-like substances. In making a comparison with these machines, one must use the same compound of such material as stearic acid, paraffin etc. Other machines are very susceptible to hardness and have different compounds pre-vulcanised or adjusted to the same modulus before a comparison is made. Finally, after laboratory tests are completed, the result should always be checked by a service comparison. No stocks have been found superior to Ureka when service tests were made.

Tear Resistance. A property of tear resistance is probably coupled up quite closely with abrasive resistance, inasmuch as the wearing away of a compound consists in the tearing out of countless very small bits of rubber compound. Here again, Ureka was found exceptionally satisfactory.

Heat Resistance. A good many rubber stocks soften seriously when operated under increased temperature conditions. Ureka is a persistent type of accelerator and does not greatly soften under high temperature work. It is unusually good therefore for large tyre and tube stocks, belting, steam hose etc.

Flexing. Present day tyre tread stocks and belt cover stocks must be made resistant to cracking, which in service frequently develops on the surface of these compounds. It has been proved that the use of Ureka in these compounds has very materially improved the resistance of these stocks to the development of cracks.

Ageing. Rubber compounders must now pay a great deal of attention to the ageing characteristics of their compounds. There are two general methods of making accelerator ageing tests, namely the Geer Oven Method, and the Bierer-Davis Oxygen Bomb Method. By either of these methods Ureka stocks will be found satisfactory. Natural ageing results over the past six years have confirmed the laboratory results obtained by both of these methods.

In conclusion, Ureka, because of its delayed action and normal curing properties, permits the use of lower temperature curing without an undue quantity of softener or milling, thereby enabling the rubber manufacturer to take full advantage of everything that low temperature cure has to offer.

Ureka White is a light greyish powder with a specific gravity of 1.37 and a melting point of about 140° C., whereas, as already stated, Ureka is a light yellow powder with a specific gravity of 1.29 and a melting point of about 125°C.

It may be summarised that both the Urekas are of the same composition, both giving as rapid acceleration as the ordinary rubber factory can handle, and yet, because of their splendidly delayed action, they may be handled by the modern higher speed machine without the difficulties so often encountered with other accelerators, giving equal vulcanisation speed.

While the vulcanisation characteristics of Ureka leave nothing to be desired, it has the unfortunate disadvantage of being unsuitable in white or very light coloured stocks. This is merely due to the fact that it contains nitro bodies which cause a yellow discoloration during vulcanisation, and that is why Ureka White has been developed to answer all the rigid requirements that the rubber manufacturer may insist upon for obtaining a product giving a pure white stock.

Let us consider now the effect of compounding ingredients with the Ureka White.

Like practically all other accelerators, Ureka White requires a certain concentration of *Zinc Oxide* to develop its full effect. The quantity necessary for most accelerators is usually a minimum of 5 parts of ordinary zinc oxide to 100 parts of rubber, although if an extremely fine or colloid zinc oxide is used, somewhat less is needed. If materially less than this quantity of zinc oxide is used, then variations in acceleration are produced according to any variations that may exist either in the quantity or in the fineness of the zinc oxide present. On the other hand, increased concentration of zinc oxide causes no change in the rate of cure, so that any quantity of zinc oxide above 5 parts per 100 parts of rubber may be added with no influence upon the cure.

Carbon Black retards the activation of Ureka White. Since standard Ureka is excellent for use in carbon black stocks and since, obviously, colour is of no consideration in these stocks, we feel that standard Ureka should be used wherever carbon black is used in high concentration. In very low concentrations such as would be used for tinting or darkening coloured stocks, carbon black has no material effect upon the rate of cure of Ureka White. If, for other considerations Ureka White is chosen for use in high carbon black stocks, then an increased concentration is necessary to overcome the retarding effect of the carbon black; in this way splendid stocks are obtained.

Stearic Acid or other fatty acids are not required to activate Ureka White. A fraction of one per cent of fatty acids is ordinarily employed in most rubber compounds to assist in dispersing pigments, and to make up for any non-uniformity in the crude rubbers. This may be used with Ureka White without material effect. Increased concentrations of fatty acids cause somewhat increased delayed action in the accelerator, but do not materially alter the final cure.

Mineral Oxides such as the inorganic accelerators formerly used, like magnesia, lime, litharge, etc., have no place in the compounding scheme with Ureka White. Accelaration is sufficiently rapid without them, and their complete elimination is recommended.

Neutral Mineral Ingredients. Most of the ordinary mineral ingredients such as are usually employed as filling materials, are neutral in effect on the rate of cure of Ureka White stocks. These include whiting (natural), barytes, blanc fixe, magnesium carbonate etc. Any quantity of these materials may be added to a Ureka White accelerated stock without materially altering the rate of cure. Very high concentrations of pigments have a slight absorptive effect, and therefore the accelerator content is usually increased to a certain extent. Various clays retard the action of Ureka White, the degree depending upon the colloidal nature of the clay used. This material occupies the position of an intermediate between the more neutral filling materials and carbon black. Increased accelerator concentration is required when a considerable quantity of clay is added to the formula.

Colours. Ureka White, being essentially a neutral accelerator, has a minimum effect on the organic colours that may be added to a compound. The result is coloured compounds of exceptional brilliancy.

Ageing. A primary consideration in the choice of an accelerator is the effect of ageing on the resultant rubber stocks. While certain accelerators, now somewhat widely used, give notoriously poor ageing rubber stocks, it is noted that rubber goods accelerated with Ureka White are highly satisfactory from an ageing standpoint. One must also bear in mind that, as a general consideration, rubber, when vulcanised with a low content of sulphur, and at a low temperature, generally has greatly improved ageing properties. Ureka White, permitting these conditions, can take advantage of this situation.

The Monsanto A-16 Accelerator. Chemically, A-16 is an aldehyde reaction product of Schiff's base. More specifically, it is an aldehyde reaction product of a molecularly rearranged and polymerized aldehyde amine, in which two different aliphatic aldehydes and aniline are the base materials.

A-16 is a further development in the series of aldehyde accelerators, the most notable examples of which have been the Monsanto A-7, A-19, and A-11.

As an aid to vulcanisation, A-16 displays universal merit. It has many advantages not shown in other accelerators. These can be briefly summarised by saying that, while A-16 is a normally handled material, it imparts tensile strength comparable to ultra-accelerators, gives an unusually long range of useful cure, provides the best of ageing—even on overcure—and is suitable for practically all types of compounds. A-16 stocks show no reversion on overcure, neither do they stiffen materially under the same conditions. This very uniform degree of hardness over a wide range of cure is a most desirable feature.

While A-16 is easily handled, it is, nevertheless, a most powerful vulcanising accelerator and produces tensile strengths in considerable excess of 4000 lbs. per sq. inch even in pure gum stocks. Good cures are obtained in a few minutes at either 40 lbs. (287° F.) or 30 lbs. (274° F.) steam, but when the temperature is reduced much below this point, the time factor is prolonged beyond normal factory practice.

Physically, A-16 is a thin brown liquid, very mobile at all normal room temperatures. It will pour quickly out of any container and no time is required for draining. The container need not be warmed at any time. A-16 accelerator, as it appears on the market, consists of two-thirds active material and one-third high boiling inert liquid diluent. This dilution is to convert the A-16 into such physical shape that will allow of ease in handling. The A-16 base alone is a viscous sticky material, having a tendency to adhere to the mill rolls. In the marketed form, however, A-16 is quickly absorbed by rubber. If added near the centre of the batch, it is all absorbed before it has a chance to run over to the roll guides. A-16 may be master-batched in the usual way, although this is not necessary. Because of its physical nature, one should not attempt more than a 10% master-batch.

A-16 may be safely handled in the factory, as it is nontoxic and gives no form of cyanosis or skin rash.

A-16 is suitable as an accelerator in all types of compounds. Because of its colour, it darkens white or light coloured stocks. However, unless a pure white or a very brilliant colour is desired, A-16 may well be used.

Zinc Oxide is a necessary catalyst with A-16, as well as most other organic accelerators. Without it A-16 shows considerable activity, but does not attain its full strength until about two parts of Zinc Oxide are present in 100 parts of rubber. To overcome varying conditions, a minimum of five parts of Zinc Oxide is recommended to 100 parts of rubber in all A-16 formulas. A further amount acts as a reinforcing ingredient only.

Carbon Black retards A-16 materially. By increasing the amount of accelerator, however, the retardation is overcome, and very good stocks result.

Clay also regards A-16, but not nearly as much as Carbon Black. Relatively slight variation in compounding will equalize these stocks.

The addition of *Lime* makes A-16 stocks more scorchy and yet does not appear to help the full cure.

The same is true of *Magnesia* in a more pronounced degree, and of *Litharge* to a lesser degree.

Therefore, the addition of any mineral accelerator is not recommended to an A-16 stock.

Softeners like Pine Tar, and Rosin, retard A-16, and proper allowance must be made in compounding.

Stearic Acid, in the concentration of one per cent of the rubber, seems to be quite neutral. Because of the possibility of deficiency of organic acids in certain rubbers, the use of stearic acid in A-16 compounds is recommended, particularly where off-grade rubbers are used. About ½% of all high grade rubber and 1½% of all wild or low grade plantation rubber are recommended. From numerous results it appears that the proper sulphur content in a compound is very close to 3.50 to 100 parts of rubber, and if any considerable amount of softeners is present, the sulphur could well be increased to about 4 00. As for the A-16, even 0.5% of the accelerator brings out good tensile, but 0.75% should be used for having its full value. Further amounts are valuable in assisting to obtain a quicker cure or to give added tensile. In the case of longer cures, however, 0.75 of A-16 is suitable for all normal purposes, and frequently less will be found to be sufficient. The lesser amounts give lower tensile and less tear resistance to the stocks. Present day tendencies are to go to the more highly accelerated or *peppier* stocks, and then cut the cost of the compound proportionately, thus showing a net saving made possible by the use of the accelerator.

Below are a few formulas, all with the Monsanto A-16 Accelerator:—

Black Sole with Reclaim.

Smoked Sheets	16	Kilos.
Whole Tyre reclaim	45	
Carbon Black	30	
Zinc Oxide	4	
Tackol	2.5	
Flectol - H	0.4	
Sulphur	1.6	
A-16	0.6	

Cure: 18 mins. at 60-lbs.

Hose Formula.

Rubber	10	Kilos.
Whole Tyre reclaim	50	
Mineral Rubber	5	
Clay	8	
Zinc Oxide	3	
Stearic Acid	0.5	
Sulphur	1.5	
A-16	0.5	

Cure: 20 to 30 minutes at 30-lbs.

Belting Cover.

Smoked Sheets	100	Kilos.
Zinc Oxide	5	
Carbon Black	30	
Tackol	2.5	
Stearic Acid	1	
Flectol - H	1	
Sulphur	3	
A-16	1.5	

Cure: 25 minutes at 35-lbs.

In concluding the theory of the Monsanto Ureka and A-16 accelerators, we should also mention that they have other accelerators, such as A-7, A-11, A-19, A-32, D. P. G., Thiotax, Thiofide, and Ureka White F, with which the rubber manufacturers should make trials for further development in the compounding process, so as to be convinced of their suitability.

Let us now consider the *Rhone-Poulenc Takars* and their similar product, the *Monsanto Ureka White F* and the *I. G. Vulkazit F*, which are replacing advantageously a wide range of other accelerators and are therefore of special interest to the manufacturer desirous of reducing the number of accelerators in use.

They are a white powder with a specific gravity of 1.31, slightly yellowish, impalpable, with a peculiar smell, and, under normal conditions of storage, are of unlimited stability. Furthermore, results from toxicological tests, to which they have been submitted, have proved that they are harmless.

We have used these accelerators for years, with increasingly satisfactory results, and we have a definite predilection for them. This being said, let us now study them further:

First, their solubility in the ordinary solvents, generally used in the rubber industry, is slight as may be seen from the following:—

Solubility in	When cold	When heated
Ethylic Alcohol	almost insoluble	1%
Benzine	1%	50%
Aceton	almost insoluble	2%
Chloroform	20%	65%

The mixings with these accelerators show no tendency to prevulcanise, either on the mixing rolls, or during subsequent processing on the calender or on the forcing machine, and are thus easily handled under all conditions. The unvulcanised stocks may be stored under normal conditions for many months. The activity of the accelerators is not impaired even if the unvulcanised compounds are stored for a considerable time.

The Vulkazit F and the Takars are delayed action accelerators, i.e. they do not become effective immediately after the curing temperature is attained. The softening and the flowing of the mixings in the first stage of the cure ensure satisfactory formation and perfect splices and seams for all moulded and press cured articles. The period of flow, which is of great importance, can be adjusted exactly to meet the specific conditions of the case in question; it can be considerably curtailed or dispensed with entirely, for hot air cures, or for the vulcanisation of such articles as tubes without insertion in talcum etc. In spite of the ease with which Vulkazit F and Takar mixings can be processed, they are active within a wide temperature range.

By suitable compounding, for example, the mixing can be made to cure in 50/60 minutes at as low a temperature as 110° C.

The curing times at different temperatures are naturally dependent on the quantities of sulphur and accelerator present in the mixing and also on the activating or retarding ingredients which may be incorporated, as will be seen later on. From the curing tests the most suitable times given for the mixings are:—

25/40 minutes at 1.5 atm.
15/20 minutes at 2.5 atm.
8/10 minutes at 4.0 atm.

Vulkazit F and Takar stocks are not only unaffected by the variations in cure which may occur under normal working conditions, but are also notable by reason of their unusually wide curing range and excellent plateau effect. It is clear therefore that Vulkazit F and Takar mixings ensure great safety and uniformity in the manufacturing process. They do not cause any discoloration of the mixings during the cure and are thus very suitable for brightly coloured and for pale transparent articles. Stocks containing these accelerators have:—

a) high tensile strength,
b) exceptionally good ageing properties,
c) no tendency to bloom with normal quantities of sulphur (2.5% and less),
d) good snappiness (high modulus) of the vulcanisates.

Goods made with these accelerators have a bitter taste and, when fresh, also have a peculiar smell. Therefore they are scarcely suitable for rubber articles for use in the foodstuff industry.

It is of great interest to rubber manufacturers that mixings containing 1% and more of Vulkazit F and Takars can be given a normal cure with a very low quantity of sulphur. On the other hand, for blooming articles, only an exceedingly small percentage of accelerator is required.

The following figures should serve as a guide for (A) Nonblooming, and (B) Blooming articles:

	(A)	(B)
Sulphur	0.5 - 2.5%	4.0 - 5.0 %
Vulkazit F or Takars	1.5 - 0.8%	0.35 - 0.30%

The above percentages are reckoned on the rubber content in the compounds.

Stearic Acid and other fatty acids, as well as the zinc salts of such acids—zinc stearate and the like—in compounds with Vulkazit F or Takars, cause delay in the commencement of cure without appreciably increasing the length of cure at 2.5 atm. They also make the goods snappier. Stearic Acid, from 0.5 to 1.5%, facilitates the handling of the mixings under difficult conditions, and whilst its use avoid the setting up on the forcing machine, it improves the storage properties of the stocks. While delaying the start of the cure at the vulcanising temperature, Stearic

Acid gives the mixings a longer softening period. It is therefore necessary, in the case of compounds cured in open steam, such as tubings without mandrel and therefore not wrapped in fabric, to use just the required quantity of Stearic Acid to give satisfactory working of the stock and to avoid the deformation of the articles. But Stearic Acid should never be used in cable stocks, or in shoe stocks to be cured in open air.

Zinc Oxide is necessary as an activator of these accelerators in all soft rubber mixings, whereas in ebonite stocks it retards the cure.

Inorganic Accelerators such as litharge, lime, magnesium oxide and magnesium carbonate, increase the speed of cure and the danger of prevulcanisation. Some care should be taken in handling stocks with these ingredients.

Brown Factice and *Alkali Reclaim* also accelerate the cure. The possibility of incorporating reclaim and factice should be ascertained in every case under the conditions prevailing.

Active Gas Black mixings require a larger quantity of Stearic Acid in order to obtain the normal tensile properties, and to reduce the tendency to bloom.

Inactive Gas Blacks bring about an unusually early commencement of cure with an increased tendency to scorch, so that difficulties in the various processing operations and on storing uncured stocks should be anticipated, if the sulphur content is not considerably reduced.

Antimony Sulphide mixings containing Vulkazit F or Takars show noticeable decrease in tensile and modulus figures, and they may give rise to factory difficulties by pre-curing on the forcing machine. So it is better not to use Antimony Sulphide but to replace it by the *Organic Dyestuffs*, which have all the desired antimony sulphide shades, so popular now-a-days, while they help to avoid all the aforesaid difficulties by assuring the safety of processing of the stocks and their storage.

From the foregoing, the manifold applications of Vulkazit F and Takars become apparent. They are excellent:

for articles cured in moulds, in direct steam or in hot air;

for rubber goods of all shades, and also for transparent products.

In conclusion, in many factories where tyres, tubes, conveyor belts, surgical goods, soles, heels and cables are made, Vulkazit F and Takars can be used as *universal accelerators*, but one important thing connected with them is that they are not suitable for rubber articles in which the soft rubber is made to adhere to metals by means of a slow curing ebonite layer, as in the case of rollers, solid tyres and the like, nor are they suitable for rubber articles used in the foodstuff industry.

To obtain a good distribution of the accelerators, Vulkazit F or the Takars should be worked into the crude rubber with the fillers, sulphur being added at the end of the mixing. The use of a master-batch of rubber with the accelerator is not recommended but for safety. Finally, mixings, when ready, should be cooled in a bath of cold water.

The Rhone-Poulenc Diphenylguanidine also called *D. P. G.* is equivalent to the *I. G. Vulkazit D.* It is a white powder, 1.13 of absolute, and 0.25 of apparent specific gravity, insoluble in water, slightly soluble in benzene, but fully soluble in ethylic alcohol, aceton and chloroform.

These accelerators are widely appreciated by rubber makers on account of their cheapness, facilities for working process, and security.

The temperature at which these accelerators start action is rather high (above 100° C), so the danger of prevulcanisation during the mixing process, calendering, or on the forcing machine is averted.

Their plateau of vulcanisation is wide, which allows the cure of articles made of thick sheets very easy. Perhaps in the case of thick rubber sheets, it is advisable to add to the D. P. G. another accelerator, as will be explained later.

The mixing with D. P. G. can be stored as long as one desires, at room temperature, the accelerator being inactive upon the mix.

The D. P. G. is harmless, does not irritate the skin of the worker, as no volatilisation occurs during any of the processes, which it undergoes. It can be preserved indefinitely, as it never oxidates and is also an *anti-resin acter.* Like the D. P. G., mixings made with this accelerator also have no smell.

The ageing properties of the accelerator are good. The improvements realised by the use of the D. P. G. are that it allows the reduction of the time of vulcanisation, the reduction in the quantity of sulphur and gives an increased nerve to the finished goods. It does not alter the conservation quality of the correctly vulcanised mixings, so it is a mistake to affirm that the *guanidines* are affecting the ageing properties of the mixings into which they are incorporated. Now the life of the mixings will still be prolonged, when the proportion of sulphur has been well established. For instance, with 3.75% of sulphur on the weight of the raw rubber, one can expect the best results. In the case of non-blooming mixings, 3.50% of sulphur should be used only, provided the vulcanisation is done at a slightly higher temperature and for a longer time.

The D.P.G., being insoluble in water, cold and hot, can be vulcanised advantageously in open steam or in water. The accelerator combines itself easily with the rubber, but care should be taken to see that it does not agglomerate during the mixing process, as it will produce spots on the finished goods.

The D.P.G. is used in the mixings in the proportion of 0.6 to 1.2% on the weight of the crude rubber, with 4 to 2.5% of sulphur. It is said that the best dose of sulphur is 3.75% with 0.8 to 1% of the accelerator. But it is necessary to include in the mixings from 5 to 10% zinc oxide; 5% would suffice when colloid zinc oxide is used. In the case of pure white mixings, 30% of zinc oxide should be used, and the proportion of sulphur should be reduced to 2%, the vulcanisation being done for 40 minutes at 3 kilos (143° C).

A master-batch is only required with the D. P. G. for having a better dispersion of the accelerator into the mixings. When making the mixing, the sulphur should be the last item to be incorporated, and when finished, the mixing should be cooled in cold water.

As for chemicals used as fillers with the D. P. G., *Zinc Oxide* is indispensable in view of good vulcanisation.

Litharge is not advisable, as it exercises a retarding action on the vulcanisation. If litharge is used, the defect may be corrected by increasing the dose of sulphur, but the finished goods will get easily torn to pieces.

Lithopone retards more or less the action of the D. P. G.

Kaolin has the same defect as Lithopone.

Factices have a retarding action still greater than the aforesaid chemicals, so in any case no more than 10% on the weight of the crude rubber should be allowed, with a slight addition of sulphur in the compound.

Carbonate of Magnesium has an accelerating action, and one can use up to 25% on the weight of the raw rubber, but then the vulcanisation should be shortened, at the temperature, say, of 135-138° C.

Calcined Magnesium is also a strong activator of the D. P. G. and the dose should not exceed from 0.5 to 5% on the weight of the crude rubber.

Oils, like linseed oil cause a certain re-action with the result that, after vulcanisation, spots are likely to appear on the finished goods.

As an example, a good mixing will be:—

Smoked Sheets	5^{k} 000
Tyre Reclaim	5^{k} 000
Zinc Oxide	0^{k} 500
Sulphur	0^{k} 500
D. P. G.	0^{k} 075

In case reclaim is used, vulcanisation should not exceed 30 minutes at 142° C, the plateau of vulcanisation being restricted. Rhone-Poulenc suggest, in case of need to associate the D. P. G. with their *Super-accelerator 501*, which is a disulfure of tetramethylthiourame, being of the same group as the *I. G. Vulkazit Thiuram*, of which some more details will be given in the following pages. The action of disulfure of tetramethylthiourame is retarded by the carbon blacks, and it is suggested that a Diphenylguanidine accelerator, which destroys the aforesaid action, should be added to the mix, probably on account of the great affinity of the carbon blacks with the Diphenylguanidine. Proceeding in this way, an excellent product resisting the traction (2^k 300 per mm^2.) can be obtained. The dose to be used is 0.5 to 0.6% of D. P. G. and 0.15 to 0.25% of super-accelerator 501, for a vulcanisation of 8 to 10 minutes at 3 kilos. Mixings composed in this way are excellent for soles, heels, technical items, hose pipes, and for the chemical industry.

The most activating proportion is obtained by 30% of super-accelerator 501 combined with 70% of Diphenylguanidine. The D. P. G. can also be associated with other accelerators of the Mercaptobenzothiazole group or the *I. G. Vulkazit Mercapto* and with the *Rapid Accelerator 201*, or its equivalent the *Vulkazit D. M.*, about which we shall discuss later on. We do not, however, think it is essential that we should enter into details about all these accelerators, for the reason that a rubber manufacturer cannot interest himself in all the products flooding the market!

Another Rhone-Poulenc product is their *Rapid Accelerator 200*, which, as already stated, is equivalent to the I. G. Vulkazit Mercapto. It is an yellowish powder with a specific gravity of 1.41. The pure product melts at 170° C. This accelerator has no smell, is almost insoluble in water, soluble with difficulty in benzene, but is soluble in aceton, alcohol, ether benzole and chloroform. Being a weak acid, it dissolves in alkalis and ammonia, forming the corresponding salts.

The Monsanto Thiotax, the Rhone-Poulenc Rapid Accelerator 200 and the I. G. Vulkazit Mercapto are chemically 2 Mercapto-Benzothiazole. Oxidation converts Mercapto-benzothiazole into disulphide, which is also well known as an accelerator, called the *Vulkazit D. M.* and its equivalent the Rhone-Poulenc *Rapid Accelerator 201.*

Mercapto-benzothiazole has a strong bitter taste, but, as has been shown several times by toxicological tests, *it is not in any way poisonous.*

The Vulkazit Mercapto, the Thiotax and the Rapid Accelerator 200 belong to the group of *semi-ultra-accelerators.* They give vulcanisates with *great tensile strength* and have a very flat curve, so that small differences in the cure have little or no effect on the goods produced. Goods cured with these accelerators have very good ageing properties.

Zinc Oxide must be added to all stocks to activate the accelerators, also 1—1.5% *stearic acid* on the weight of the rubber. In *gas black* mixings, the amount of stearic acid should be increased from 2 to 3% according to the amount of gas black present.

These accelerators do not discolour the rubber goods made with them, either during the cure or on subsequent exposure to light, and are therefore very valuable for making white and pale coloured articles.

With the usual amounts of sulphur and accelerator, non-blooming vulcanisates are obtained in 20—25 minutes at 42 lbs. (= 142.8° C). By the use of a basic accelerator, in addition to the Rapid Accelerator 200, Thiotax or the Vulkazit Mercapto, the duration of the cure can be appreciably shortened and the temperature of vulcanisation considerably reduced. The most valuable second accelerators in order of increasing activity are D. P. G., Vulkazit F. P., Vulkazit 1000, Vulkazit D., and Vulkazit H (but it must be remembered in this connection that the latter can cause a skin rush on specially sensitive persons; so for light coloured bed-sheetings, air pillows and the like, it is better to use Vulkazit 1000). Others of the Vulkazit range such as *Vulkazit Thiuram*, *T. R.*, and *576* are also powerful activators for Thiotax, for Vulkazit

Mercapto and Rapid Accelerator 200, so much so that it is essential to reduce the amount of sulphur and accelerator. The *critical temperature** (say the makers of the Vulkazits) is lowered to a varying degree by the addition of these accelerators. By the addition of the correct amount of suitable accelerator to the rubber compound the effect of an ultra-accelerator can be obtained. Such combination is consequently specially suitable for *the cure in hot air.*

A part of the quantity of Vulkazit Mercapto, or of Thiotax, or of Rapid Accelerator 200 given in the mixing can be replaced by Vulkazit D. M. or Rapid Accelerator 201. This will not in any way alter the properties of the articles so produced, but the stock becomes much more easy to handle, and it may be stored without trouble.

As articles made with either Vulkazit Mercapto or Thiotax or Rapid Accelerator 200 have the same bitter taste as the accelerators themselves, they are *not suitable for use* where they might come into contact with *foodstuffs.*

The action of the fillers on these accelerators can be described as follows:—

Zinc Oxide is indispensable for good activation, the usual dose being 5% on the weight of the crude rubber.

Stearic Acid is required for the full action of these accelerators and also to dissolve the zinc oxide so as to enable the latter to produce its full activation power. At least 1.5% on the weight of the raw rubber should be taken in the ordinary mixes.

In the transparent compounds 1% should be taken only with the combination of colloid zinc oxide. On

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* The author has explained on page 36 what he thinks about the critical temperature of any accelerator.

the contrary in mixings with gas blacks 3—4% are required.

Litharge, Lime & Magnesia are activators of these accelerators and for this reason they should be avoided, as they increase the danger of pre-vulcanisation.

Antimony Sulphide is not altered by these accelerators.

Brown Factice, and alkaline reclaims are slight activators of these accelerators, and when mixes do contain a large quantity of these products, care should be taken to prevent pre-vulcanisation.

White Factice has a retarding effect on these accelerators as is generally the case with all accelerators.

Kaolin has not got a retarding effect on vulcanisation when it is used with a minimum of at least 2 % of stearic acid calculated on the weight of raw rubber in the compound.

Dyestuffs usually used in the rubber industry can be used with these accelerators.

When only normally activated stocks with Thiotax, or Vulkazit Mercapto or Rapid Accelerator 200 are made, they are handled in the usual way, the sulphur or the accelerator being added at the end of the milling or even when warming up. Under these conditions it is worth while using a *master-batch* in order to ensure rapid and even distribution of the small quantity of accelerator.

Strongly activated stocks containing accelerator combinations are prepared on rolls which are kept well cooled and which are adjusted, so that the rubber is about 6mm. thick on the front roll. After the mixing is completed, the rubber is taken off in sheets of the same thickness. To ensure *rapid cooling* of the sheets, they should be thrown into cold water, and it is absolutely essential not to fold and store the sheets whilst they are still hot. The uncured stocks containing Thiotax, or Vulkazit Mercapto or Rapid Accelerator 200 tend to bloom. This can be avoided by the following means:

Adding the sulphur during warming up, using well masticated raw rubber, using well cooled rolls for mixing and rapidly cooling the finished mix. The running of the stock on the *calender* or *forcing machine* can be carried out without difficulty if the usual precautions for accelerated stocks are observed, and an addition of a softener is an advantage, as it enables the calender bowls and the forcing machine to be kept at a lower temperature, which avoids the danger of scorching during the run. The use of Vulkazit Mercapto or Thiotax or Rapid Accelerator 200 is recommended for the following articles, amongst others:

1. For treads and carcasses for motor car and motor cycle tyres.

2. For bicylcle tyres; for red, white and transparent treads, the best results are obtained with these accelerators plus Vulkazit H, which gives the short cure desired for moulded articles.

3. For motor and cycle inner tubes.

4. For technical and surgical articles of all kinds such as gas tubings, irrigator tubings, hose pipings, compressed air, brake, and other special pipings, belts; quick curing moulded goods, such as air cushions, hot water bottles and the like.

5. For rubber shoes cured in hot air, Vulkazit Mercapto, Thiotax, or Rapid Accelerator 200 and their combinations with basic accelerators are specially suitable. Combinations of Vulkazit Mercapto or Thiotax or Rapid Accelerator 200 with Vulkazit D are very

useful for moulded soles and heels in view of getting harder stocks and shorter cures.

6. For driving and transporter belts of which the cure can be carried out quickly and at low temperature, which is specially recommended for the preservation of the fabric against the prolonged action of steam. We give below, as an example, a mix for manufacture of crepe soles:

Pale Crepe	10^{k} . 000	
Colloid zinc oxide	0^{k} . 100	
Sulphur	0^{k} . 250	
Rapid Accelerator 200 or Vulkazit Mercapto or Thiotax	0^{k} . 090	
Diorthotolylguanidine	0^{k} . 025	(A Rhone-Poulenc Accelerator)
Stearic Acid	0^{k} . 100	

Cure: 10 minutes at 142° C.

Proceeding with the wide range of Accelerators, we wish to consider in a few lines the particulars regarding the Rhone-Poulenc *Rapid Accelerator 201* and its equivalent, the I. G. *Vulkazit D. M.*

They are yellowish odourless powders with no particular taste, practically insoluble in water, alcohol and benzine; in other common solvents their insolubility varies between 0.5—1%. Their specific gravity is 1.45. The following notes will outline the *chief properties and advantages* of the Vulkazit D. M. and the Rapid Accelerator 201 when incorporated in rubber mixes:

1. *Compounds with these accelerators cannot prevulcanise on milling, calendering, or tubing, and do not self-cure even upon prolonged storage.*

The use of these accelerators prevents delay and trouble even under unfavourable conditions during processing operations. No loss of material occurs due to pre-vulcanisation of mixes with Vulkazit D. M. or the Rapid Accelerator 201, and the machines can be run at full capacity.

These accelerators may be considered absolutely safe and reliable even for use in the tropics.

2. *Compounds with Vulkazit D. M. and Rapid Accelerator 201 do not begin to cure until some time after they reach the vulcanisation temperature.*

During the first part of the cure, the stock softens, which is desirable for:—

(*a*) *Moulded goods and those made in the press.*

No pre-vulcanisation takes place through contact with hot moulds or press plates during the time required to fill the moulds and close the presses, so no folds arise through bad flow of the rubber. No open seams or joints in balls, bulbs or other hollow articles are to be feared.

(*b*) *Goods with Insertion.*

To ensure that the fabric is thoroughly impregnated with rubber before vulcanisation commences.

3. *When Vulkazit D. M. or Rapid Accelerator 201 are used, there is no discoloration of the mixes during the cure or on exposure to sunlight.*

Bright shades can be obtained with only small quantities of dyestuffs.

4. *Mixes with these Accelerators cure quickly* (25—30 minutes at 3 atm.).

The time of cure can be shortened without danger by adding to these accelerators other suitable ones.

5. *Non-blooming articles are obtained with the usual quantities of sulphur and accelerator.*

A mixture of these accelerators with Vulkazit H or with Vulkazit D gives non-blooming vulcanisates in 15—20 minutes at 3 atm.

6. *Mixes with Vulkazit D.M. or Rapid Accelerator 201 can be cured at a pressure of 2 atm. and upwards,* and at still lower temperature, if a second accelerator is used.

7. *Mixes with these accelerators age very well.*

8. *They are easily and readily incorporated into the rubber.* They show no tendency to stick to the walls or to form lumps, so uniform distribution of the accelerator is obtained.

9. *Toxicological tests have shown that these accelerators are completely harmless and non-poisonous.*

10. *Goods manufactured with them possess a characteristic smell and taste.*

They cannot, therefore, be used for rubber goods which are likely to come into contact with foodstuffs.

Tests should be carried out on simple Vulkazit D. M. or Rapid Accelerator 201 mixes with the addition of different raw materials, in order to ascertain the influence of these additions on the cure. The results will serve as a guide to the Rubber Chemist in the working out of mixes with these accelerators.

Inorganic accelerators, such as litharge, magnesia, lime and magnesium carbonate, bring about a more rapid vulcanisation of the mixings. Pre-vulcanisation takes place at 110° C. with litharge and magnesium carbonate, and it is to be expected when using rather larger quantities of lime and magnesia.

Alkaline Reclaims. Even small quantities of reclaim shorten the time of cure and increase the tendency of the mixes to vulcanise at 110° C. The possibility of using mixes containing a high percentage of reclaim must be ascertained by work's tests. It has thus been established that more suitable accelerators for mixes containing large quantities of reclaim, or made with reclaim alone, are *Vulkazit C. T.* and *576.*

Vulkazit D. M. or Rapid Accelerator 201 mixes can be worked with safety with the addition of *Aldol-alphanaphtylamine powder*, which is an active anti-oxidant.

Antimony Sulphide. When running Antimony Sulphide mixes on the forcing machine, difficulties may occur through pre-vulcanisation. Antimony Sulphide shades can be matched by using organic pigments, and such mixes have no tendency to scorch where Vulkazit D. M. or Rapid Accelerator 201 is used either alone or in combination with Vulkazit H.

Brown Factice. Vulkazit D. M. and Rapid Accelerator 201 mixes with up to 20% Rape Oil factice show no tendency to scorch when run on the forcing machine. The possibility of using mixes with a high factice content should be ascertained by work's tests.

Gas Black. Normal tensile strength will be obtained by adding a higher percentage of stearic acid (3—5% in stocks containing gas blacks).

Stearic Acid. In all mixes containing these accelerators, 1—2% stearic acid should be used (reckoned on the raw rubber content in the mixes).

The addition of stearic acid delays the action of accelerators at the temperature of vulcanisation without noticeably altering the length of the cure.

The vulcanisates are snappy which means higher tensile strength, elasticity and less elongation.

By using Vulkazit D.M. or Rapid Accelerator 201, solely or with Valkazit H, red and light coloured transparent treads can be obtained by all cures of practical duration. Red and transparent bicycle tubes can be worked without difficulty on the forcing machine. We give below a formula for red treads:

Red Treads.

110.0	Pale crepe.
90.0	Red motor tube waste.
3.5	Sulphur.
10.0	Zinc Oxide.
10.0	Lithopone.
1.5	Ozokerite.
1.5	Stearic Acid.
8.0	Mineral Oil.
30.0	China Clay.
70.0	Chalk.
2.0	Vulcan Red D. K. F. Paste.
1.2	Vulcan Orange G. Extra F. Paste.
1.2	Vulkazit D. M. or Rapid Accelerator 201.
0.3	Vulkazit H.
0.8	Aldolalphanaphtylamine Powder.

(All the above weights are in kilograms).

Cure : 10 minutes at 3½ atm.

Vulkazit D. M. and Rapid Accelerator 201 are the most suitable accelerators for ball mixes, because :

1. Stocks with these accelerators are soft and can be easily moulded during the first phase of the vulcanisation, that is, when the maximum pressure is exerted by the inflating material. Thus complete and invisible joining of the seam is always obtained.

2. Light coloured balls can be obtained by using Vulkazit D. M. or Rapid Accelerator 201. No discoloration takes place during vulcanisation, or on exposure to light.

3. These accelerators, do not affect varnish on painted balls, or the enamel on bulbs.

4. Anti-oxidants cannot be used in ball stocks owing to both the discoloration in light, and to the bad influence on the drying and adhesion of the varnish.

Therefore the good anti-oxidant effect of Vulkazit D. M. or Rapid Accelerator 201 is especially valuable.

In conclusion, Vulkazit D. M. and Rapid Accelerator 201 have proved satisfactory under the most difficult working conditions met with in the cable industry.

No pre-vulcanisation on the forcing machine.

Good ageing after 21 days at 60° C. without the use of an anti-oxidant.

A further advantage in using Vulkazit D. M. or Rapid Accelerator 201 in coloured cable mixes is that only small quantities (0 5—1 %) of organic dyestuffs are necessary.

The Rhone-Poulenc *Rapid Accelerator 501* and its equivalent, the *Vulkazit Thiuram,* come next in our discussion of accelerators used in the rubber industry. The I. G. Thiuram, the Monsanto Thiuram D. S., the Ultra Zinc D. M. C., and Ultra D. M. C., all these accelerators should be grouped in the same category, since they are all products derived from dimethylamine, all of them providing accelerators of the ultra type.

Chemically, Thiuram D. S. is Tetramethylthiuram Disulphide, Ultra D. M. C. is Dimethylammonium dimethyldithiocarbamate, and Ultra Zinc D. M. C. is the zinc salt of the previous acid, or a zinc dimethyldithiocarbamate.

Practically all rubber manufacturers agree that the lesser the amount of sulphur one has in a stock, the better will be the ageing and heat resisting properties of that stock. The Thiuram group provides sulphur in a highly active form by decomposition at the curing temperature, and it has been realised that very much less of this active sulphur is required for vulcanisation, than if simply sulphur was added to the mix in the ordinary way. By this, one obtains really *phenomenal* *ageing results* together with very little tendency to reversion, and so, by proper compounding, one is sure of obtaining a very satisfactory heat resisting stock.

Of course, the use of the Thiurams is only of interest in the specialised field, as it is a relatively expensive method of vulcanising rubber.

The accelerators we are now discussing are of a white yellowish powder with a specific gravity of 1.46. Chemically pure substance melts at 150° C. They are soluble in Acetone, Ether, Benzole, Chloroform, Carbon Bisulphide, Carbon Tetrachloride and hot Alcohol. Their solubility in Benzine (petroleum) is very slight and they are practically insoluble in water. They have a neutral reaction and are not hygroscopic. When stored under ordinary conditions, they keep perfectly well. According to toxicological tests, the small amounts which have to be used are *harmless.*

These accelerators belong to the class of *Ultra-Accelerators.* Thiuram stocks can be handled on the mixing rolls and calender without any special difficulty, and—if certain precautions are taken—can be run on the forcing machine. Stocks with the Thiurams can be cured in the *press* as well as in *steam* or in *dry air.* The lower the temperature at which the cure is carried out, the better are the properties of the vulcanisates. The difficulties in manufacture, such as rapid burning and bad flow in the moulds, which can readily occur with many ultra accelerators of the dithiocarbamate group, are avoided by the use of the Thiurams.

Vulkazit Thiuram and Rapid Accelerator 501 are the best accelerators for making non-blooming stocks which will cure quickly at low temperatures. They are excellent for making pure white or brilliantly coloured articles. Remarkably transparent vulcanisates can be obtained by using them with a small quantity of zinc oxide active (0.5 to 1% on the weight of the rubber).

Freshly cured Thiuram stocks have a faint smell which *disappears on storage.* Rubber goods made with them have no unpleasant taste like those made with many other accelerators, and are therefore excellent for use where they may come into contact with *foodstuffs*, that is to say for bottle rings, beer and wine hoses, and the like. Thiuram stocks have *very good ageing properties.* In order to fully develop their activity, Vulkazit Thiuram and Rapid Accelerator 501 need an addition of zinc oxide to all mixes. Usually 5 to 10 parts of zinc oxide are added to each 100 parts of rubber.

Stearic Acid should be added to all stocks containing these accelerators to an extent of 0.5 to 1% on the weight of the rubber. The addition of stearic acid gives *snappier* vulcanisates and makes the stock easier to handle.

As in the case of other accelerators, the activity of Vulkazit Thiuram and Rapid Accelerator 501 is affected by the *addition of a second accelerator.* Of those which have an *activating effect, the basic accelerators* Vulkazit H, Vulkazit D and Vulkazit 1000 are most useful. The combination of the Thiurams with Vulkazit H is best for transparent goods. Quite small quantities of Vulkazit H have an appreciably lightening effect on the shades of the vulcanisates.

Of as great interest as the activating substances, are those bodies which have a retarding effect on the vulcanisation. Litharge is suitable for this purpose, but for its poisonous properties, which prevent its incorporation in stocks to be in contact with foodstuffs.

Whilst Litharge delays the commencement of the cure, its duration is considerably lengthened, and there is a tendency to blooming even after long cures, the tensile strengths also being reduced.

Furthermore, the discoloration of the vulcanisates by the lead sulphide formed during vulcanisation prohibits the use of litharge in white and pale coloured articles.

Vulkazit D. M. and Rapid Accelerator 201 are excellent in combination with the Thiuram stocks, as even a small amount of these accelerators has a retarding effect on the commencement of vulcanisation.

By suitably adjusting the amounts of Vulkazit Thiurm and Vulkazit D. M. or Rapid Accelerator 201 with Rapid Accelerator 501, absolute *safety in handling* and storage of stocks can be attained, as these accelerators have *no discolouring effect* on the goods whatever. The addition of Vulkazit D. M. and Rapid Accelerator 201 to Vulkazit Thiuram or Rapid Accelerator 501 stocks improves their ageing properties considerably. The combination of the aforesaid accelerators, Rapid Accelerator 201 plus Rapid Accelerator 501, is therefore of special interest for the manufacture of *pure white and brightly coloured rubber goods*, primarily for *quick curing moulded articles*, for stocks to be run on the forcing machine, for all kinds of transparent goods, also for cut sheets, proofing, for the continuous vulcanisation of rubber flooring, rubber mats and the like.

Vulkazit D. M. and Rapid Accelerator 201 also retard or prevent pre-vulcanisation *in rubber solution* containing Vulkazit Thiuram or Rapid Accelerator 501.

As to the quantity of accelerator required, 0.2 to 0.5% Vulkazit Thiuram or Rapid Accelerator 501, and 2.0 to 2.50% sulphur calculated on the weight of the rubber is generally used. With larger amounts of Vulkazit Thiuram and short cures, blooming of the stocks sometimes occurs. An addition of Vulkazit D. M. or Rapid Accelerator 201 in such stocks will prevent this blooming.

Mixes with *3 to 4 parts of Vulkazit Thiuram or Rapid Accelerator 501*, to 100 parts of rubber can be cured *without sulphur.* Such stocks are safe to handle. The vulcanisates have wonderful ageing properties, and are remarkably *resistant to heat*, either dry heat or steam. For rubber goods which are to be exposed to heat, the best stocks are those with a high content of Vulkazit Thiuram or Rapid Accelerator 501 with either no sulphur or not more than 5% sulphur on the weight of the rubber.

When Vulkazit Thiuram or Rapid Accelerator 501 stocks are being worked, great care must be taken to observe all the precautions usually prescribed for powerful accelerators:

1. It is best not to add the accelerators direct to the mix, but to add it in the form of a master-batch containing 1 part accelerator to 9 parts rubber.

This will ensure rapid and perfect distribution of the small quantity of accelerator. The master-batch is added either at the end of the mixing process or immediately after the mastication of the rubber. In the latter case, the sulphur is added either after all the constituents have been incorporated or better still during warming up.

2. Vulkazit Thiuram and Rapid Accelerator 501 stocks must be prepared on *well cooled rolls.* The temperature of the mix is kept down by suitably adjusting the rolls. It is generally advisable so to adjust the rolls that the rubber is not more than six m. m. thick on the front roll.

3. The stock is also taken from the rolls in sheets about 6 m. m. thick and at once cooled. The sheets of

rubber should not be put together or piled up before they have become quite cold. If the sheets are folded or stored while still hot, difficulties will arise in the subsequent handling. In order to cool the sheets more rapidly as they are taken from the rolls, it is an excellent method to immerse them for two or three minutes in cold water.

4. When the stock is run on the forcing machine, the jacket and screw must be well cooled.

The die must be only warm enough to enable the stock to have a smooth surface.

5. Waste from the calender and forcing machine must be sheeted out thinly and well cooled.

6. The rolls should be set closely during warming up so as to get rapid softening without developing too much heat.

7. Stocks containing ultra accelerators should not be stored for several weeks before being used up.

As *methods for reducing temperatures* during mixing and subsequent working of Vulkazit Thiuram and Rapid Accelerator 501 stocks, it is recommended:

1. *An addition of water during the mastication* of the rubber (3 to 5% on the weight of the rubber). The evaporation of the water carries off the heat, and a more intensive mastication of the rubber occurs, causing the stocks to become more softened and more plastic.

2. The use of plasticisers keeps down the temperature during mixing and subsequent working and so reduces burning.

Of the many articles for which Vulkazit Thiuram and Rapid Accelerator 501 can be used with advantage, the following are some of the more important:

1. Mechanical goods of all kinds: these accelerators being the best ones for the mass production of all kinds of moulded goods, as they allow short cure for non-blooming goods.

2. Rubber sheets: in the manufacture of galoshes Rapid Accelerator 501 or Vulkazit Thiuram offers the following advantages:

Low temperature of vulcanisation (115 to 125° C.)
Short Cures (90 to 60 minutes).
No tendency to bloom.

3. Articles to be in contact with foodstuffs such as bottle rings, wine and beer hoses and the like can be made in bright colours by the use of vulcan dyestuffs.

Antimony Sulphide should not be used to colour Vulkazit Thiuram or Rapid Accelerator 501 stocks, as it increases the tendency to scorch.

Transparent articles can be produced with only a short cure at a lower temperature by the use of Vulkazit Thiuram or Rapid Accelerator 501 and zinc oxide active.

4. Bathing caps, with the use of these accelerators, can be produced in brilliant colours or in fashionable shades, either in the press or in open cures.

5. Hot water bottles: Vulkazit Thiuram and Rapid Accelerator 501 give the desired short cure, freedom from blooming and good ageing.

6. Flooring and matting: Vulkazit Thiuram or Rapid Accelerator 501 plus small amounts of Vulkazit D. M. or Rapid Accelerator 201 is specially recommended to give odourless quick curing stocks; no difficulty in working or storing, good flow and the best colours.

7. Proofed Fabrics, such as waterproofs, bedsheeting, motor hoods and the like can be cured with

Vulkazit Thiuram or Rapid Accelerator 501 in hot air at 115 to 120°C.

8. Very transparent dipped goods can be made with these accelerators. A small addition of Vulkazit D. M. or Rapid Accelerator 201 will prevent jelling of the solution.

9. Sponge rubber can conveniently be made with the combination of Vulkazit Thiuram and Vulkazit D. M. or Rapid Accelerator 201. Short cures can be given, and the long softening period as well as the delay in commencement of vulcanisation ensures satisfactory blowing of the mix, that is to say, heat resisting stocks are made with larger quantity of Vulkazit Thiuram or Rapid Accelerator 501, without sulphur. There is no difficulty in working such a stock, and no danger of overcuring.

Ebonite can be made with Vulkazit Thiuram or Rapid Accelerator 501 at low temperature with short cures.

It should be borne in mind that the increasing of the quantity of accelerator speeds up the cure and gives snappier vulcanisates. The samples cured for 45 minutes at 7 lbs. or for 10 minutes at 25 lbs. show no trace of curing up, but one should remember that with lower curing temperature, tensile strength and modulus are increased.

Stearic Acid additions increase the strength and modulus of the Rapid Accelerator 501 and Vulkazit Thiuram stocks. These stocks are more easily handled at lower temperature.

Inorganic Accelerators, such as magnesia, magnesium carbonate and lime cause vulcanisation to commence much more quickly. Lime also appreciably lowers the tensile strength.

Litharge, which retards scorching in amounts below 0.5%, has the opposite effect in large quantities and also lowers the strength.

Stocks containing *reclaim or factices* start to cure more quickly, and they cannot be handled or stored easily. It is necessary to make tests on a Work's scale to find out if these stocks can be handled safely.

Carbon Blacks of various kinds, such as gas and oil blacks, absorb Rapid Accelerator 501 or Vulkazit Thiuram as they do other accelerators. The amount of accelerators must be increased considerably to obtain good tensile strength. By the use of a second accelerator, such as Vulkazit D. M. or Rapid accelerator 201, vulcanisates with excellent properties are obtained.

It is to be noted that a combination of Vulkazit D. M. or Rapid Accelerator 201 with Rapid Accelerator 501 or Vulkazit Thiuram is of great value for gas black stocks giving stiffer and stronger valcanisates.

Antimony Sulphide should not be used with these accelerators. The colour of antimony sulphide can be produced with vulcan dyestuffs without any difficulty arising in storing or handling of the stocks. In addition, articles made with vulcan dyestuffs can be produced in much brighter colours.

Vulkazit 1000 strongly activates Rapid Accelerator 501 or Vulkazit Thiuram stocks, and these stocks are of special interest, as they have only *a very faint smell.* In fact the makers do not say much about their Valkazit 1000, and all that the author can certify is that it is a very good accelerator for combination with other accelerators, that it is a perfect accelerator for compounds to be in contact with foodstuffs, but being extremely volatile, the said Vulkazit 1000 affects the nose, inducing sneezing by all those in the vicinity of the roller on which the compound with that Vulkazit is made.

Aldolalphanaphthylamine Resin causes the earlier start of vulcanisation.

M. B. is the best non-discolouring anti-oxidant for use in Vulkazit Thiuram or Rapid Accelerator 501 stocks.

The addition of small quantities of litharge to stocks containing zinc oxide and Vulkazit Thiuram or Rapid Accelerator 501 greatly slows down vulcanisation. Larger quantities such as 5% on the rubber cause vulcanisation sooner than when no litharge is present.

With litharge the vulcanisates have lower tensile strength and greater tendency to blooming. Larger addition causes a noticeable darkening of the stocks owing to the formation of lead sulphide.

Ebonite can be made with Vulkazit Thiuram or Rapid Accelerator 501 using either at a low temperature or higher temperature and short cure. A high percentage of zinc oxide is useful to assist the cure in this case.

With these accelerators Ebonite can also be cured in hot air or in boiling water.

Rapid Accelerator 501 or Vulkazit Thiuram is of great value for all articles which may come into contact with foodstuffs. The articles can be brightly coloured, or be quite transparent. As an example, a mixing is given below:—

Floating Red stock for bottle rings, wine and beer hoses and the like:

Pale Crepe	100^{k} 0
Zinc Oxide	3^{k} 0
Titanium Dioxide	1^{k} 5 to 2^{k} 5
Sulphur	2^{k} 5
Ozokerite	0^{k} 8
Paraffin (Medicinal)	1^{k} 0 to 2^{k} 0
Stearic Acid	0^{k} 5 to 1^{k} 0

Vulkazit Thiuram or Rapid Accelerator 501	0^{k} 250
Vulcan Orange G. Extra F.	2^{k} 0
Vulcan Rubine B. K. F.	0^{k} 550

Cure: 20 minutes at 28 lbs. (=132.8° C.)

Mixing for Hot Water Bottles:

Pale Crepe	100^{k} 0
Zinc Oxide	10^{k} 0
Whiting	30^{k} 0
Titanium Dioxide	3^{k} 0
Paraffin Wax	0^{k} 5
Mineral Oil	1^{k} 5
Sulphur	2^{k} 250
Vulkazit Thiuram or Rapid Accelerator 501	0^{k} 250
Vulkazit D. M. or Rapid Accelerator 201	0^{k} 150
Anti-Oxidant R. R. 5	1^{k} 5
Vulcan Orange G. Extra F.	1^{k} 0
Vulcan Rubine B. K. F.	0^{k} 3
Stearic Acid	0^{k} 5

Cure: 11 minutes at 35 lbs. (132.8° C.)

Mixing for sponge rubber mats:

Pale Crepe	100^{k} 0
Zinc Oxide	5^{k} 0
Sulphur	2^{k} 5
Vaseline	8^{k} 0
Vulkazit Thiuram or Rapid Accelerator 501	0^{k} 1
Vulkazit D. M. or Rapid Accelerator 201	0^{k} 2
Sodium Bicarbonate	5^{k} 0—10^{k} 0
Stearic Acid	5^{k} 0— 8^{k} 0
Titanium Dioxide	5^{k} 0

Vulcan Dyestuff	....
Anti Oxidant M. B.	1^{k} 0

Cure in the press: 30 minutes at 7 lbs. and 25 minutes at 39 lbs. (141° C.), the height of the mould being 1″.

Accelerator *Vulkazit P Extra N* finds its applications in the ordinary mixes and in latex mixes as well. In this chapter, we shall only consider its uses in compounds made of crude rubber and ingredients.

This accelerator is the zinc salt of ethylphenyldithiocarbamic acid. It is a yellowish white powder without taste or odour, the specific gravity of which is 1.46. The chemically pure substance melts at 205° C., the technical product at 204° C. It is an accelerator of neutral re-action in limited stability and non-hygroscopic. Both the accelerator itself and goods made with it are completely harmless. The Vulkazit P extra N is soluble in various organic solvents such as benzole, chloroform, carbon tetrachloride etc. Its solubility in benzine, acetone, and ethyl alcohol is very limited, whilst it is practically insoluble in water.

The Vulkazit P Extra N must be considered as an ultra-accelerator. It differs from the usual accelerators of the dithio-carbamate class, in that it enables mixings to be handled safely.

Handled with reasonable care, the mixings can be worked without difficulty, they may be stored with safety for months, and solutions of Vulkazit P Extra N mixings in benzine are stable for weeks.

Rubber articles made with Vulkazit P Extra N are quite non-toxic, and the latter gives the palest vulcanisates which can be obtained with accelerators of this class. This also applies to transparent goods. Articles made with Vulkazit P Extra N are completely tasteless and practically odourless. In this respect Vulkazit P Extra N is superior to all non-staining accelerators. Depending upon the type of article and the conditions of cure in question, the quantity of accelerator varies between 0.3% to 1 %, and the quantity of sulphur from 2.4 % to 1.8 %, reckoned on the rubber content of the mixes. The quantities of sulphur and accelerator given in some examples of mixes hereafter are intended to serve as an indication for the different types of stocks.

Vulkazit P Extra N is equally suitable for cures in the press, in open steam, in hot air and in water. The curing temperatures and times, using ordinary proportion of sulphur and accelerator, are approximately the following:—

For dipped goods cured in water: rubber solution with benzine, about 30—50 minutes at 85 to 95° C.

For dipped goods cured in hot air: rubber solution with benzine, about 45—50 minutes at 110° C.

For Proofed Fabrics cured in hot air: rubber solution with benzine, 40—50 minutes at 110° C, or 25 to 30 minutes at 120° C.

The curing conditions for moulded articles and for rubber goods cured in steam, vary naturally depending upon the thickness of the articles and the size of the form. In fixing the cure, it should be considered that the curing limits of Vulkazit P Extra N mixes at higher temperature are relatively narrow. Thus it will be seen that thick walled articles such as bottle rings, codd rings and the like cannot be vulcanised uniformly at higher temperatures, than at 1.0 to 1.5 atm.

The increased stability of Vulkazit P Extra N rubber solutions with benzine renders possible the rapid and cheap process for heat cured dipped goods, in which many manufacturers have so often expressed a special interest.

In proofed fabrics, the sufficient degree of stability of the rubber solution with benzine and the low vulcanisation temperature make Vulkazit P Extra N an ideal accelerator for this purpose. The necessity of using two solutions, one containing the accelerator and the other the sulphur, as is the usual practice when other ultra-accelerators are used, is avoided in the case of Vulkazit P Extra N.

Also the safety in processing and the good storing properties of mixes containing Vulkazit P Extra N, in addition to the rapid commencement of cure, render it the most suitable accelerator in the manufacture of bathing shoes, bathing caps and similar products.

For rubber containers for foodstuff and other articles which must be odourless and tasteless, Vulkazit P Extra N is certainly the most interesting accelerator, as it meets the requirements of uses of this type of articles, which formerly could not be fulfilled.

Vulkazit P Extra N is unsurpassed as an accelerator for all pure white and light coloured articles, as well as pale transparent goods, in addition to odourless and tasteless articles.

In processing Vulkazit P Extra N mixes, the same precautions naturally hold good as are usually applied when working with fast accelerators. The mixes must be made on well cooled rolls. The rolls should be set, so that the thickness of the rubber around the rolls does not exceed 6 mm. The raw rubber should first be masticated thoroughly on cold rolls, possibly with the addition of a little water in order to ensure safe working, particularly on the forcing machine. The approximately 6 mm. thick sheet cut off from the rolls should be immediately cooled by dipping in cold water.

To ensure good distribution of the accelerator, this should be mixed in with the other compounding ingredients. The separately weighed sulphur should either be added at the end of the mixing process or during the warming up.

The extruding of the mixes on the tubing machine should only be carried out with a well cooled jacket, a cold screw and a cold or only slightly warmed head. The die should only be warmed up to the degree necessary to ensure the obtaining of a smooth surface.

Scrap from the forcing machine and from the calender must be sheeted out rapidly and thoroughly cooled.

Mixes containing ultra-accelerators should not be kept for weeks before being further processed.

The safety against scorching exhibited by Vulkazit P Extra N is great. By small additions of a second accelerator, the mixing can be regulated as to satisfy practically all working conditions. To retard the setting up of the mixes, Vulkazit D. M. is more suitable, but a combination of Vulkazit D. M. with Vulkazit Thiuram can be used, and Vulkazit Mercapto is also suitable to delay the commencement of vulcanisation.

Stearic Acid facilitates the processing of the mixes and yields rather snappier vulcanisates. In the case of hot air cures, the vulcanisation is delayed, and for this reason such stocks should be made without, or with only a small quantity of, stearic acid.

We give below a few examples of mixes with Vulkazit P Extra N accelerator.

1. For Foodstuff container accessories such as bottle rings and the like:

Pale Crepe	100^k 0
Zinc Oxide Special	4^k 0
Sulphur	2^k 4

Stearic Acid	1^{k} 5
Ozokerite	0^{k} 5
Paraffin Oil	1^{k} 0
Aldolalphanaphthylamine Powder	0^{k} 4
Vulkazit P Extra N	0^{k} 4
Vulkazit DM or Rapid Accelerator 201	0^{k} 050
Vulkazit Thiuram or Rapid Accelerator 501	0^{k} 050
Cadmium Red G	2^{k} 0

Cure in steam: 5 minutes rise to attain 1.5 atm. Maintain for 15 minutes. Then reduce to 1.0 atm. and maintain for 18 to 20 minutes.

Cure in water: 5 minutes rise to attain 1.5 atm. and maintain for 30 to 35 minutes.

Another mix for cycle valve tubing:

Pale Crepe	100^{k} 0
Zinc Oxide Active	1^{k} 0
Stearic Acid	1^{k} 0
Ozokerite	0^{k} 6
Paraffin Oil	1^{k} 5—2^{k} 0
Vulkazit P Extra N	0^{k} 320
Vulkazit DM or Rapid Accelerator 201	0^{k} 060
Vulkazit Thiuram or Rapid Accelerator 501	0^{k} 060
Sulphur	2^{k} 4
Anti Oxidant MB	0^{k} 3
Magnesium Carbonate	4^{k} 0

Cure in talc: about 20 minutes at 2.0 atm. 134° C.

Rubber solution with benzine containing Vulkazit P Extra N can be kept for several weeks without setting up, provided that no alcohol is added to the solution, as this causes rapid prevulcanisation.

The following is a mix for dipped goods:

Pale Crepe (well masticated)	100^{k} 0
Zinc Oxide Active	0^{k} 8
Sulphur	2^{k} 2
Vulkazit P Extra N	1^{k} 0
Vaseline Oil	2^{k} 0

Cure in hot air: 45—50 minutes at 110° C.

Another mix for surgical gloves:

Pale Crepe (well masticated)	100^{k} 0
Zinc Oxide Active	0^{k} 6
Sulphur	1^{k} 8
Vulkazit P Extra N	0^{k} 8
Vaseline Oil	2^{k} 0

Cure in water: about 30 minutes at 95° C.
Cure in steam: about 25 minutes at 110° C.

Vulkazit P Extra N is also of great interest to the manufacturer of proofings, as the mixes and their solutions in benzine have good storage properties and furthermore the proofed fabric can be vulcanised at low temperatures.

Following is a mix for proofed fabrics:

Smoked Sheets (well masticated)	100^{k} 0
Gas Black	6^{k} 0
Factice Gloria	6^{k} 0
Whiting	100^{k} 0
Sulphur	2^{k} 2
Zinc Oxide Special	5$_{k}$ 0
Vulkazit P Extra N	1^{k} 0
Vaseline Oil	2^{k} 0

Cure in hot air: 40 minutes at 110° C.

In concluding the chapter on Accelerators, we might say that we have samples of bicycle tubes vulcanised with Vulkazit F in 1933, in Karachi, and these samples are still, in 1942, in every good condition. We may also state further that we have produced in 1935, in the Travancore Government Rubber Factory, solid tyres using Monsanto's Urekas. These tyres, which were then fitted to the wheels of the Golden Chariot of His Highness the Maharaja of Travancore, are still in perfect condition in 1942. We also produced in 1935 in the same factory, with Ureka, Mottled Carpets, which can still be seen in excellent condition on the floor of the dining room of the Mascot Hotel, Trivandrum, where they have now been in use for seven years!

CHAPTER VI.

Chemicals used as Fillers in Rubber Compounds.

IN the foregoing chapter, we have considered the action of some chemicals upon the vulcanisation of rubber compounds, when the latter are combined with accelerators.

In this chapter, we shall consider more fully these chemicals, which are called *Fillers.*

What are Fillers? They are small or large quantities of finely ground substances which are present in most rubber articles. Ever since the inception of the rubber industry, attempts to introduce various *Minerals* into rubber mixes have been made in a purely empirical way, with the only object of arriving at a cheaper cost price of rubber compounds, and it may be asserted that no pulverised substance exists which has not been tried in the rubber industry. But since the day the rubber manufacturer has learnt to examine the influence of the fillers, by laboratory tests, most of the fillers of olden days have now disappeared, and those which have been maintained are classified under three distinct categories:

(*a*) *Minerals* used as fillers with the only object of reducing the cost price of the compounds, called *Inactive Fillers;*

(*b*) *Minerals* acting as accelerating agents, called *Pigments;* and

(*c*) *Minerals* which enhance the properties of hardness, flexibility, resistance to wear and tear, and ageing of the rubber compounds, such fillers being called *Active Fillers.*

With regard to inactive fillers, they all impair the mechanical properties of the rubber, and their incorporation into the rubber compound is only justified where a definite and notable reduction in the price of the article is desired. Many factors have to be considered before arriving at a final decision as to the kind of filler to be adopted, the cheapest filler by weight being not always the cheapest by volume, which is indeed a very important factor to be considered, since the rubber maker invariably buys the raw material by weight, whereas he sells the finished product by piece.

The first duty of the Rubber Technologist is then to build up his rubber compounds in such a way—while bearing in mind the purpose for which they are intended—as to produce goods of the lightest possible specific gravity, reducing thereby the price per volume as far as possible.

Another factor is the consideration of the case where the filler has to act as a pigment, for obtaining a white stock, for example. In this instance, the Rubber Chemist should know that the quality of a white mineral depends not always upon its covering power, when applied in the form of a coating to a non-transparent base, but on the coefficient and refraction of the mineral used in the rubber. It has been established that rubber has a coefficient of 1.525, lithopone 2.30, zinc white being approximately of the same magnitude, and titanium dioxide 2.71. So, these fillers can be called highly colouring pigments, whereas such fillers as barytes, having a coefficient of only 1.637, chalk of 1.658 and kaolin of 1.53, do not colour the rubber at all. In thin layers, mixtures made of 100 parts of rubber with 40 parts of these non-colouring minerals will remain transparent. Unfortunately, these substances are inactive, whilst zinc white is not, and the only defect of this fine, white, and active pigment is that it is an expensive chemical. Another fairly active non-colouring filler is *Colloid Kaolin*, but it has a very serious drawback in that it is not compatible with most of the present day accelerators.

Then there is *Silicious Chalk*, another filler of importance, comparatively cheap in price, with a specific gravity of 2.22, which may be considered relatively low when compared with the barytes, the specific gravity of which is 4.5.

Actually there is no such product as *Silicious Chalk*. It would be more accurate to call it *Fire-Clay* and the analysis given hereafter is just a typical one of a fire-clay with high silica and low calcium alkali contents. A standard analysis result for a fire-clay of definite composition is also not existing, as it has been proved that various samples of fire-clay, coming from the same source, when analysed, show a composition which varies within fairly wide limits.

We are, however, adopting the denomination *Silicious Chalk* as it is the name given by the suppliers of these fire-clay products, which even in large quantities do not impart any colour to the rubber compound.

From several investigations on the part of the author, as well as the accumulation of proofs shown in leaflets from the Neuburg Firm (a few extracts from which are quoted elsewhere in this book) he has come to the definite conclusion that the said product is the ideal active filler which can be incorporated in any mix with any of the existing accelerators, and so he has adopted Silicious Chalk in most of his formulas, as will be seen in the following chapter.

In the case of quite white articles, he has used only Silicious Chalk with a small addition of lithopone bronze seal, or titanium dioxide, which mixture was found far superior to, and cheaper than, the one produced only with lithopone red seal, of low percentage, from a qualitative point of view.

Silicious Chalk exerts no influence whatsoever upon vulcanisates, whether in retarding capacity or in accelerating manner, and when on the mixing roller, or on the calender, it does not agglomerate in lumps.

There is still another factor to be considered, which speaks again in favour of the use of Silicious Chalk, namely the calender effect. Since most of the manufactured articles are produced from thin calendered sheets, say on an average of 1 mm. thick, it has been proved that the tensile strength and ductility in these sheets are greater in the longitudinal direction than transversally. It is this phenomenon which we call the *calender effect.* A proof of this can be seen when a cut, made at right angle in a fresh calendered sheet, opens out into the longitudinal direction if torn further. This is due to molecular process, and the colder the calender roller for calendering the rubber sheet, the more noticeable will the phenomenon be. But the temperature at which a sheet can be drawn on the calender depends, however, solely upon its quality, and rubber filled with inactive minerals will not stand any drought temperature, as the mixture would then turn sticky and pasty. Experience has made it clear that a mixture in which Silicious Chalk has been incorporated can be drawn without hesitation at a roller temperature of from 80 to 100° C., the calender effect at such temperature being no longer noticeable. To be on the safe side, it is suggested that, with a view to facilitate the further manipulation of the rubber sheets, they should always be allowed to hang for a few days so as to re-establish the nerve of the rubber, inevitably reduced by the calendering process. Silicious Chalk can be incorporated in coloured compounds as it does not affect the shades of them in any way, since its mechanical behaviour in connection with rubber and any adjunction is absolutely neutral.

Tests effected in the author's laboratory have demonstrated that Silicious Chalk improves the tensile strength of the rubber compound and ameliorates its flexibility to pull and compression. It assures hardness, when desired, resistance to wear, tear, fatigue, and hysteresis. It can be said that Silicious Chalk is an adequate filler for a number of rubber compounds as it is absolutely acid-proof like the barytes, and can under the circumstances be used in mixes which have to resist to any action of the acids.

In cold vulcanisation also, the use of Silicious Chalk has proved very satisfactory.

Silicious Chalk is a diatomaceous earth or an infusional earth, principally obtained from places between Hamburg and Hannover, where large deposits have been found and worked. The following is the result of the analysis of Silicious Chalk:

SiO_2	(Silica)	....	80.670
Al_2O_3	(Aluminia)	....	8.961
Fe_2O_3	(Ferric Oxide)	....	0.435
CaO	(Calcium Oxide-lime)	....	0.540
K_2O	(Potassium Oxide)	....	2.784
Na_2O	(Sodium Oxide)	....	....
MgO	(Magnesium Oxide)	....	1.679
Loss on ignition		....	4.931

Kieselgurr is of almost the same composition as Silicious Chalk, as may be seen from the following analysis:

SiO_2	(Silica)	65 to 87%
Al_2O_3	(Aluminia)	2 3 to 11.7%
Fe_2O_3	(Ferric Oxide)	3 to 11.7%
CaO	(Calcium Oxide or lime)	in small proportions.
MgO	(Mangnesium Oxide)	
K_2O	(Potasium Oxide)	
Na_2O	(Sodium Oxide)	5 to 14%

Carbon Black in the past was only a mere black dye for rubber compounds, but opinion has changed since then, and now-a-days, every rubber manufacturer is convinced that Carbon Black is a filler having various properties. It has been found that there are *active* gas blacks which require, in the process of mixing, larger quantities of stearic acid, in order to obtain normal tensile properties, and to reduce the tendency to bloom, whereas *inactive* gas blacks (also called *Soft Blacks*) cause an unusually early commencement of cure with an increased tendency to scorch, so that difficulties in the various processing operations and in storing uncured stocks should be anticipated, unless the amount of sulphur has been considerably reduced. Active and Inactive Gas Blacks are numerous, as in the case of accelerators, and all that can be said is that now-a-days compounding practice is complicated, the resulting demands of the compounder being so extremely technical that the rubber manufacturer is bound to be perplexed, as he cannot reasonably assimilate into his fabrication the various gas blacks with which the market is now flooded, all of them having more or less determined action upon the rubber vulcanisates.

In deciding on the type of Carbon Blacks to be used, whilst their dispersing properties are of prime importance, there are various other qualities which the rubber compounder requires to know. One of these is the influence on the rate of cure exercised by the more or less volatile content of the blacks and their accelerator absorption tendencies, a minimum degree of accelerator absorption being essential for a rapid cure of the rubber compound.

All these factors have been taken into account in the following descriptions of Carbon Blacks, which we think will be of interest to the rubber compounder.

The Dixie Gas Carbon Blacks are fillers which give a compound of excellent tensile and good modulus properties. The rate of cure with these kinds of Carbon Blacks is rather faster than with other blacks, the optimum *tensile* being attained with normal acceleration for about 45/65 minutes. The *hardness* obtained is also a little more than that obtained with other Carbon Blacks, whereas the *plasticity* has been developed with Dixies, combining both high modulus and easy processing properties, the dispersion of the Black into the mixture being excellent, and it has been found that Dixie Gas Carbon Blacks are suitable for all qualities of tyre compoundings with a degree of hardness in the cured tread commensurate with maximum wear.

The Thermax Carbon Black, a soft thermatomic carbon, is another product of which much can be said. Many people associate the use of natural gas carbons in rubber with stiffness and lack of resilience in the finished product. To produce resilience or rubberiness, they generally use mineral fillers.

While it is true that some forms of carbon black—the channel blacks—are noted for their stiffening and deadening effect, it should not be forgotten that, by other means of gas decomposition, blacks are being made which show none of the characteristics of channel blacks, but resemble the mineral fillers in their compounding properties. Thermax is one of these products.

Thermax can replace many mineral fillers in a great variety of compounds, with production of greater resilience, better strength and tear resistance, and equally good ageing quality. It has also the advantage of low volume cost.

It is a form of finely divided carbon obtained by thermal decomposition, or cracking of natural gas under suitable temperature conditions. It is not black, but dark grey in colour; and stocks made with it are of dark grey colour, not jet black like channel black stocks.

The advantages of Thermax in compounding rubber are numerous, the more important being:

low volume cost,
high loading capacity,
good tensile quality,
low stiffening and low modulus,
high resilience,
good heat resistance,
aids extrusion and calendering, and
tends to accelerate the rate of cure.

The low specific gravity and low volume cost of Thermax make it an ideal material for the loading of a great variety of inexpensive articles with simultaneous production of much better physical quality than can be obtained from whitings, clays, barytes and other similar materials. Perhaps the greatest field of usefulness for Thermax is in dark coloured, high grade mechanical goods of all kinds. As a highly resilient filler, it is excellent in black automobile inner tubes, in tyre carcass and cushion stocks.

Due to its high loading capacity, Thermax is very useful in heavily loaded stocks, such as oil-resisting goods and flexible tyre bead compounds, where the use of large volumes of low-cost mineral fillers lowers the physical strength and tear resistance of the stocks too much. The following is a partial list of goods in which Thermax may be used to advantage:

> Mechanical goods, Passenger Inner tubes, Tyre carcass, Tyre Cushions, Tyre bead wire covers, Tyre curing bags, Oil-resisting stocks, Footwear, Wire and Cable covers, Hose of various kinds, Heat-resisting articles.

Other varieties of Blacks are:—

The *Micronex Beads*, which are the original *dustless* form of active Carbon Black. They can be used for both *black and coloured stocks.* Micronex Beads have a soft centre or core with a tougher shell, which makes them truly dustless. The initial pressure upon them in the mixer puts the beads promptly and completely into dispersion.

Fumonex, or *Castex*, is a softer black than Micronex. It does not possess the same reinforcing properties as Micronex, but it is very desirable for use in certain kinds of rubber compounds. Fumonex gives high resilience and easier mixing and extrusion properties than can be obtained with other reinforcing agents. Fumonex is to be used in the production of all rubber hoses for gardens, because a high percentage of Fumonex can be incorporated in that type of compound, giving a resilient rubber mixture so much desired in that particular item. It is also used in the manufacture of Gasoline-Resisting Specialities, Automobile Specialities, Hydraulic Rubbers, Steam-Resisting Goods, Belting and Packing and Cover Stocks for Insulated Wires and Cables.

Velvetex is a black used primarily as a rubber filler. It should be noted that Velvetex contains a tarry softener, and in using this black, the softener content should be reduced proportionately. As Velvetex is used as a filler, it is of particular interest to the rubber industry, when crude rubber prices are high.

Velvetex has been successfully used in the production of soft tyre frictions, and for rubber mattings or other articles where a cheap compound is desired.

There are other types of Carbon Black: *Gas-Black-P-33*, for example, which is a trade name for an *inactive* gas black, and the *Carbon-Black-Arrow*, which is an active black of the Micronex type. But once again, it is left to the rubber manufacturer to determine the choice of his chemicals, as no suitable advice can be given on this important question of adopting one Carbon Black in preference to another.

Zinc Oxide. The next chemical we shall have to consider is Zinc Oxide.

As in the case of the Carbon Blacks, we may repeat here that the reinforcing properties of this chemical are a function of the size of its particles. For instance, Ordinary Chalk (Whiting), Natural Barytes and Kaolin or China Clay are perfectly inactive, whereas Precipitated Chalk, Precipitated Barytes, which, is the same as *Blanc Fix*, and Colloid Kaolin, have a certain strengthening effect. It is also the case with Zinc Oxide, the strengthening factor being dependent on the size of its particles, and Zinc Oxide obtained by distillation of Zinc will not strengthen as much as the substance obtained from Zinc Hydroxide.

Zinc Oxide in its active form will harden considerably less. Products made with it are very flexible, and tensile strength and resistance to wear and tear are less than when combined with Carbon Black. Its specific gravity is considerably high, and accordingly the price per volume is bound to rise appreciably. In articles which in service are likely to become very warm, like solid tyres, the value of Zinc Oxide is indisputable, owing to its good conductivity of heat.

The following is the analysis of Zinc Oxide:

	Red Seal.	*White Seal.*
Pb (lead)	0.20	0.27
Fe (iron)	0.003	0.01
Cd (cadmium)	0.07	0.07
As (arsenic)	no trace	no trace
Sb (antimony)	....	....
Cu (copper)	....	....
S (sulphur)	0.06	0.06
H_2O (water)	0.05	0.07
Loss on calcination	0 10	0.25

Zinc Oxide is now largely used in every rubber compound, as it is a very activating agent in mixtures combined with accelerators.

Zinc Oxide Active, which is a colloid form of the American *Kadox*, is a highly active filler, with no colouring power. It has its applications as follows:—

(a) *As an easily soluble Zinc Oxide* (say 0.25 to 8.0% on the rubber) for transparent or semi-transparent rubber goods of all kinds;

(b) *As an antisoftener* (5 to 12% on the rubber) for mixes which tend to deform easily, especially for hot air cures like thin-walled tubes, balls and the like;

(c) *As a fatigue inhibitor* (8 to 35% on the rubber) for improving resistance to fatigue of rubber, especially in addition to inactive Zinc Oxide or blacks, when specially good mechanical properties are required: for motor tubes, carcass stocks, friction, solid tyres and rollers of all types;

(d) *As a reinforcing pigment* (30 to 75% on the rubber) for white and light coloured stocks, to improve resistance and hardness for soles, heels, buffers, special tubes and hard rollers.

Zinc Oxide Special is a product which has the following properties:

(a) *As Accelerator Activator*, it strongly increases the accelerating effect by small additions, and prevents retardation of cure owing to freedom from acid and ingredients which retard vulcanisation.

(b) *As a filler (in concentration of over 10% on the rubber)*, it has a *uniform distribution*, with *no marked softening effect* on the uncured stocks; produces *increased hardness* (modulus) on the vulcanised mix in comparison with the ordinary Zinc Oxide;

(c) Needs *slightly lower curing temperature*, compared with the ordinary Zinc Oxide;

(d) Has normal ageing properties.

The next chemical to be mentioned is the *Sulphur* used in the form of Flowers of Sulphur. This chemical is the vulcanising agent to be combined with the accelerators. It is a yellow fine powder of 300 mesh, and acid proof.

Precipitated Sulphur, notwithstanding the fact that it has a more active action upon vulcanisation, is rarely used in rubber compounds.

Chalk, also called carbonate of calcium, whiting and silicate of magnesium, are inert products only used as inactive fillers in rubber compounds.

Light & Calcinate Magnesium, also called carbonate of magnesium, is a light accelerating agent with a toughening effect on the rubber compound.

Litharge has been analysed as follows:—

Fe	Iron	0.008%
Pbo	Monoxide of Lead about	99.88%
Zn	Zinc	Traces
Al	Alumine	Traces

This product is no more used in rubber compounds in combination with most of the existing accelerators for reasons already given in the foregoing pages.

Blanc Fix, Sulphate of Barium and Lithopone are also inert products used as fillers. Sulphate of Barium is specially used in acid-resisting compounds. As for Lithopone, also called Titanium Dioxide, this chemical is produced by precipitated Sulphite of Zinc and Barytes.

Oils. Besides Cycline, of which mention has already been made in Chapter IV, there are other oils which are used as softeners, for instance linseed, castor, and rape oils.

A good mineral oil for rubber mixes should be solube in benzene, alcohol, ethers, acetones, and have the following properties:

Specific gravity of about	0.925	at 15° C.
Viscosity	6.5 Engler	at 50° C.
Melting Point	200° C.	
Flash point	200° C.	
Freezing Point	—15° C.	

Oils are never used in mixes which have to resist steam, and in those to be exposed to humidity. To ascertain whether the vulcanised rubber is free from oil, a sample of it is allowed to stand for four hours in an oven filled with humid heat at 325° F. If there is oil in the rubber compound, the sample would not stand the test.

Waxes and Paraffins. These are mostly used in mixes for the forcing machine, as they help the extruding of rubber compounds, while a smooth surface is given to the products.

Minium of Lead, composed of Peroxide of Lead—PbO_2—28.30% and Tetroxide of Lead—Pb_3O_4—72.70%, was used in the past in steam-resisting mixes. It is light pink in colour, which changes to black after vulcanisation. Now-a-days on account of accelerators, this product is used rarely.

Stearic Acid and Stearic Oil are used in combination with accelerators as explained in the foregoing pages.

Wiener Chalk is a vulcanising activator.

Mineral Rubber or Bitumoid is a fatty black product incorporated into the rubber compound to facilitate its extrusion on the forcing machine.

Mica-Dustex is a filler used in the storage of battery cases, for dusting raincoat fabrics and electrical gloves.

Kaolin, also called Dixy Clay, China Clay and Titanium Chalk, is an inert filler. Care should be taken, as there are various qualities of Kaolin which can affect the cure of the rubber compound, as has been seen in the chapter on Accelerators.

Antimony Sulphide or Golden Antimony. These are dyes of various shades which were used in the past. There are two grades: those which contain no sulphur, and those which contain a certain amount of free sulphur, the latter helping the vulcanisation of the rubber compounds in which they are incorporated. The product is mainly a mixture of:

Antimony Trisulphide	$Sb_2 S_3$ and
Antimony Pentasulphide	$Sb_2 S_5$
with a Specific Gravity of	2.5 to 2.9

Since many accelerators do not combine with Antimony Sulphide, the latter is no more in use in the rubber compounds, its shade being advantageously replaced by the organic dyestuffs, of which the combined shades are able to give Antimony Sulphide colours, so much appreciated in the rubber industry.

Rubber Dyes. They are now all of organic composition. Those of German origin are the Vulcan dyes of all shades, whereas the Monsanto dyes are the Red IE, Orange 15E, Blue 12E etc

Iron Oxide, (Fe_2O_3) is a valuable pigment without action upon accelerators and unaffected by the vulcanisation process. It contains about 98% oxide and has a specific gravity of between 5.0 and 5.2.

Factices are rubber substitutes and are of different grades: White and Brown Factices, Gloria Factice, White Rheinau Factice etc. They are generally a sulphurised rape oil free from chlorine, containing no ash. Now-a-days due to new vulcanisation methods, the slow working of white factice has proved unsatisfactory, and as most of the accelerators do not agree with compounds in which this factice is incorporated, the latter is not now largely used in rubber compounds. In cases where white factice is to be added to the compound, it is essential to incorporate also a sufficient quantity of Magnesium Oxide in order to neutralise the effect of the free acid, formed during vulcanisation, which would otherwise destroy the action of the accelerator. In fact in the past on account of their low prices, compared with the price of raw rubber, they were the real substitutes for rubber, which they replaced in remarkable proportions in the composition of the mixes. But now their employment is only justified in compounds requiring a surface feel and in compounds for printing rollers, the main object of which is the absorption of the printing ink. No doubt, suppliers of factices will maintain that their products assimilate themselves freely with accelerators of all kinds, that the use of factices ameliorates the resistance of the rubber goods to the effect of light, but all this is subordinate to the trials which the rubber manufacturer may make in his laboratory, which will be his best guide for the adoption of these products.

Rubberol Perfumes from the Monsanto Laboratories are thick viscous oils free from water, with a specific gravity of 0.985 at 15° C. They are unaffected by cold or hot vulcanisation and have no influence whatever on the ageing properties of the rubber goods. By using Rubberol Perfumes, it is possible to hide the smell of the vulcanised rubber goods and to impart to them a smell similar to the original perfume.

The requisite quantity of Rubberol depends upon the size and shape of the articles, thickness of the walls or layers and also on the composition of the mix and the nature of the accelerators used. It is therefore not possible to give exact figures, particularly as the nature and intensity of the same is a matter of personal taste. As an indication, from 20 grams to 0.2% on the weight of the rubber mix may be used.

The following are the various Rubberol brands:—

Rubberol	A	Belles fleurs.
,,	B	Lilas.
,,	C	Pine Needle.
,,	D	Violettes.
,,	E	Cyclamen.
,,	F	Millarom.

We give below the specific gravity of various chemicals used in rubber compounds:

Ammonia Bicarbonate	1.57
Aerfloted Carbon Black	1.75
Asbestine Dust	2.70

Atmido white fossil flour	2.00
Bitumoid softening pitch	1.06
Barytes double refined	4.20
Ceresine Wax	0.93
Cadmium Yellow	4.80
Chrome-Lead-Yellow & Orange	6.29
Chrome-Oxide-Green	5.21
Durabol Phenylamine	1.04
English Brilliant Red Oxide	5.20
Extra Barytes	4.20
Heavy calcined Magnesia	3.20
Glas flour	2.60
Iron Oxides, All shades	5.20
Italian Red	5.20
Kaolin Stiffening Filler	2.60
Lithopone	4.20
Litharge	9.28
Lime	2.22
Lamp Black	1.90
Lead White	6.27
Magnesium Carbonate	2.22
Mica Flakes	3.00
Naphtaline Wax	1.02
Paraffin Wax	0.93
Paraffin Oil	0.90
Petralatum	0.90
Quick Lime	2.20
Rosin Oil	0.98
Rosin	1.08
Red Lead	8.20
Slate dust	2.60
Substitutes, Brown & white	1.08
Sulphur Aerfloted	2.00
„ Sublimed	2.00
Stearic acid	1.00
Talc	2.74

Talite white fossil flour	2.00
Titanium Clay	2.58
Titanic white	3.70
Ultramarine Blue	2.35
Vermilion	9.20
Vulcan colours	4.20
Whiting	2.67
Whiting precipitated	2.70
White Lead	6.27
Zinc Chromate	5.57
Zinc Stearate	3.00
Zinc Oxide	5.57
Zinc Sulphide	3.50

CHAPTER VII.

Reclaimed Rubber.

NOW that the price of raw rubber has risen considerably, *Reclaimed Rubber* will again be made use of in increased quantities. It is quite obvious that the chief reason for its use is the lower volume cost of rubber compounds containing it. There are various types and grades of reclaimed rubber, the best and most widely used being the reclaim obtained by the *Alkali Process.*

By this method, relatively finely ground scrap rubber containing fabric, is subjected, in a vulcaniser of the Hermann Berstorff type (see fig. II), to a temperature of about 200 lbs. steam pressure over a period of several hours, during which time it is continually stirred in a solution of sodium hydroxide of about 5% strength. When this digestive period is over, the material is dumped on a screen where it is thoroughly washed, first of all to remove the excess alkali, and secondly, to remove the hydrocellulose which is formed as a result of the hydrolysis of any cotton fabric present. Certain poorer grades of alkali reclaim have the hydrocellulose put back into them, primarily to reduce the weight-cost of the product. But better grades have this material entirely washed out.

A second method for reclaiming waste rubber is the *Acid Process.* This method is more commonly adopted in cases where unvulcanised or semi-vulcanised scrap, such as tyre fabric trimmings or mould overflow, is available. Such scrap is gathered in bundles and placed in an open lead-lined tank where it is treated with dilute sulphuric acid for several hours at a temperature somewhat below the boiling point. This does not result in much alteration to the rubber itself, but does completely hydrolyse the fabric. Subsequent washing, similar to that given to the alkali reclaim, removes the excess acid and the hydrocellulose formed. The resultant rubber, if unvulcanised tyre trimmings are used, is quite soft and plastic, and makes an excellent material to go back into friction stocks. The rubber value of such a reclaim is quite high inasmuch as the rubber has not been previously vulcanised and is hardly what would properly be termed *reclaimed rubber.* It might be more appropriate to call it *Recovered Rubber*, if we use the term *reclaim* in a general sense as meaning rubber that has previously been vulcanised.

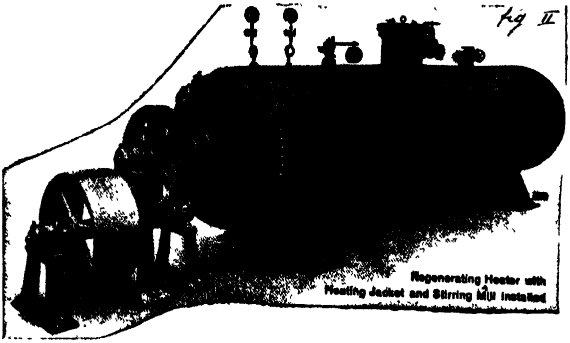
The third type of reclaimed rubber is obtained by the *Oil Process.* In the manufacture of this type, scrap, which does not contain any fabric, is selected. It is ground quite fine and mixed with from 10 to 15% of various oils, or resin-like materials, and heated in steam for several hours, the steam pressure varying from 60 to 120 ℔s.

All three types of reclaimed rubber are milled after manipulation. This smooths out irregularities caused by semi-reclaimed lumps usually found here and there throughout the product. Certain qualities are strained in special forcing machines, so as to remove foreign material such as bits of metal and so forth. Better grades are refined by passing through a Heavy Duty Mill, set to produce a very thin sheet and with the rolls running at a ratio of 1:5. This tends to grind out any lumps of material, and also permits coarse or bad material to be worked to one side.

The chief source of raw material for the rubber reclaimer is *discarded automobile tyres.* Generally, the wire beads are cut off and the rest of the tyre is ground up and made into reclaimed rubber. Such a grade is known as *Whole Tyre Reclaim.*

SPECIAL REGENERATING VULCANISER WITH HEATING JACKET COMBINED WITH A STIRRING MILL FOR THE PREPARATION OF RECLAIMED RUBBER.

Fig. II.



Sometimes the treads are stripped off and reclaimed separately, and then we have *Tyre Tread Reclaim* and *Tyre Carcass Reclaim.* Solid tyres may be reclaimed separately, and discarded air bags from tyre factories, provide a very cheap grade of stock, since the rubber content has been very severely heated during its normal life.

Footwear, hose and other miscellaneous articles, all provide types of reclaim, but the volume of this scrap available is very small in proportion to the amount of tyre scrap available, and hence reclaim made from these articles is somewhat more expensive. Inner tube reclaim can be made from the waste of tubes. These may be classified as *Floating* and *Non-floating* types, as well as *Red*, *Black* or *Grey* types. The floating variety now commands rather a high premium, as the amount of scrap available is rather small. Likewise, the red inner tube reclaim is somewhat limited. This colour very largely disappears during reclaiming, and the product has to be brightened by the reclaimer after his transforming operations.

White Reclaim is decidedly a thing of the past. While there are a number of white rubber articles on the market, the collection of sufficient scrap of white rubber is indeed too expensive a problem. So called white reclaim available today is generally reclaim made from any pure gum scrap and coloured white, or closely approximating to that colour, after the reclaiming operation. A certain amount of white scrap may be mixed with it during reclaiming.

Vulcanised reclaimed rubber has neither the tensile strength nor the extensibility of compounds made with new rubber. Consequently, it should be used where these two physical properties are not demanded in a large measure. Any rubber article that is not subject to considerable extension and is not subject to abrasive wear can probably be very satisfactorily made from a compound consisting of a large quantity of reclaimed rubber. Such articles as the cover and tube of rubber hose, rubber bumpers or vibration absorption pads, soles, heels, and various technical articles of all kinds can be made from compounds containing a large percentage of reclaimed rubber, and perfectly satisfactory results obtained. There are other articles in which reclaimed rubber cannot be used to advantage. For instance, all light-coloured rubber compounds prohibit the use of reclaimed rubber; and all highly extensible stocks must be made entirely from new rubber. These include such articles as rubber thread, elastic bands, toy balloons, rubber gloves etc. Where tear-resistance is an important factor, reclaimed rubber is not very satisfactory. Hence hot water bottles, and similar items are usually made from new rubber only.

Reclaimed rubber can be used in tyre manufacture, but certain limitations should be pointed out. Exhaustive work on the use of reclaimed rubber in treads shows that while satisfactory tread stocks can be made with reclaimed rubber, the drop in the mileage figure obtained is greater than the drop in the total cost of the tyre. Hence, it is uneconomical to use reclaimed rubber in tyre treads, and it can more satisfactorily be used in tyre carcass stocks, as in the latter the function of the rubber compound is essentially to keep the individual cords apart and to prevent them from rubbing against each other, the resultant friction finally causing separation and bursting. Reclaimed rubber can fulfil this function almost as well as raw rubber, and hence in tyres employing considerable reclaimed rubber, it will be found that the amount used in the carcass stocks will be two or three times as much as the amount used in tread stocks.

The use of reclaim is tied up with the relative cost of raw rubber and reclaimed rubber. Of course, when raw rubber is higher in cost, the selling price of reclaim is also increased. The substitution of reclaimed rubber for raw rubber can be made not only on the basis of reduction of material cost in the final product, but also on the basis of reduction of factory working costs. Even with raw rubber at the low figure of annas two per pound, reclaimed rubber can still be used to a certain extent. This is because its use in certain articles is fully as satisfactory as new rubber, and its processes through the factory ensure much less consumption of power and greater ease of extrusion than is the case with new rubber. Its vulcanisation characteristics are different, and it permits quick press cures with less difficulty and with less irregularity than when using new rubber.

When we consider the vulcanisation characteristics of reclaimed rubber, it is necessary also to consider the types of reclaims to be used. The use of acid reclaim is relatively small and it is proposed to eliminate this from our discussion, except for the brief remark that users of this type of reclaim should be very careful to see that the acid is thoroughly washed out from the product and to make note that even when this is thoroughly done, the character of the resulting stock is generally acidic, and has a retarding action on the accelerator used in the mix. Of course this can be overcome by slightly increasing the accelerator, but acid reclaim should not be added to the stock without checking this point thoroughly.

The addition of oil reclaims to stocks necessitates considerable increase in the sulphur content of the mix. Not only do oil reclaims bring in the mix considerable oil and resinous matter added to reclaimed rubber, but the rubber itself would seem to be of such a nature as to require a higher coefficient of vulcanisation than new rubber vulcanised with ordinary accelerators.

Since the bulk of reclaims used is "Alkali Reclaim", our remarks on vulcanisation characteristics refer to this type. Alkali reclaim is fast curing, compared with new rubber, and its reaction with different accelerators varies considerably. For example, the *Monsanto Thiazole Accelerators* in pure rubber stocks are relatively slow, but the alkaline characteristics of reclaimed stock speed up the cure materially, so that reclaimed rubber stocks, accelerated with either *Thiotax*, *Thiofide*, or any of the *Urekas*, are quite fast curing, particularly the first two. Alkaline stocks, accelerated with the *Aldehyde Accelerators*, such as the *Monsanto's A-7*, *A-11*, *or A-16*, give lower modulus and more rubber-like stocks than when Thiazoles are used. The rate of cure of the Aldehyde stocks is slightly slower than the Thiazole stocks, with the exception that the faster *Aldehyde Accelerator A-32* has a speed of cure very much the same as the Thiazole accelerators.

If high modulus, stiff stocks, and particularly fast curing stocks are desired, the Thiazole type accelerator should be used. If relatively low modulus, more extensible stocks and somewhat moderate cures are desired, the Aldehyde accelerators A-7, A-11 or A-16 should be adopted, and for characteristics between these two, A-32 is an excellent accelerator.

If long life is desired in reclaim stocks it is well to use an anti-oxidant. It is well known that the oxidation of rubber is auto-catalytic, and since reclaimed rubber is partially oxidised, the tendency for it to oxidise further is accelerated. Like other antioxidants, the Flectol B and H have the same antioxidant effect in reclaimed compounds. B should be used where a certain softening effect is desired, remembering that H is somewhat easier to handle, as it is a powder.

As an indication, we give hereafter a few typical formulas, with additions of reclaim, as suggested by Monsanto. These formulas are largely made using a standard grade *whole-tyre-reclaim* such as is produced by nearly all reclaim factories. Lower grade reclaims can be used with proportionate reduction in the physical properties to be obtained. If *oil-reclaims* are substituted, correction will have to be made in the sulphur and accelerator contents, and both these figures will have to be increased to provide a satisfactory cure. If *tube-reclaims* or *tyre-carcass-reclaims* are used in place of the *whole-tyre-reclaim*, there will be less compounding effect, and more rubber content will be introduced by the use of these reclaims. Consequently, sulphur and accelerator ratios will likewise have to be increased somewhat.

Tread stocks with Reclaim. On the following pages are figures illustrating the effect on tensile strength, elongation and modulus of increasing amounts of reclaim added to *Ureka tread stocks:*

	A	B	C	D	E	F	G	H	J	K	L	M
Smoked Sheets	54	54	46	46	40	40	33	33	25	25	15	15
Whole Tyre Reclaim	10	10	20	20	30	30	40	40	49	49	60	60
Carbon Black	24	24	22	22	21	21	19	19	17	17	14	14
Zinc Oxide	6	6	5	5	4	4	4	4	4	4	4	4
Stearic Acid	1	1	1	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tackol	1.4	1.4	1.4	1.4	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	2.125	2.125	2.06	2.06	2.0	2.0	1.9	1.9	1.8	1.8	1.65	1.65
Ureka	0.65	0.75	0.6	0.7	0.6	0.75	0.55	0.7	0.5	0.65	0.4	0.5

Stock	**Cure**	**Modulus at** 300%	500%	700%	**Tensile @ Break**	**Ult. Elong.**
A	30′/20 lbs.	761	1950	3485	3715	730
B	-	992	2400	4135	4380	725
C	-	887	2120	3640	3835	725
D	-	1045	2465	4050	4090	710
E	-	853	1925	-	3000	690
F	-	1038	2225	-	3065	650
G	-	775	1735	-	2560	650
H	-	913	2020	-	2875	645
J	-	740	1525	-	2165	645
K	-	891	1817	-	2475	635
L	-	480	940	-	1300	660
M	-	539	1075	-	1543	665
A	60′/20 lbs.	1524	3365	-	4910	680
B	-	1750	3765	-	4870	625
C	-	1335	2925	-	4255	665
D	-	1480	3180	-	4545	655
E	-	1300	2750	-	3720	650
F	-	1540	2950	-	3478	585
G	-	1230	2470	-	3130	615
H	-	1435	2800	-	3320	600
J	-	1030	2025	-	2515	615
K	-	1260	2460	-	2850	600
L	-	697	1335	-	1725	605
M	-	819	1595	-	1890	575
A	90′/20 lbs.	1800	3695	-	4950	630
B	-	1935	4060	-	4890	595
C	-	1515	3325	-	4200	600
D	-	1780	3580	-	4225	580
E	-	1290	2780	-	3665	605
F	-	1565	3040	-	3380	530
G	-	1280	2590	-	3190	605
H	-	1405	2800	-	3250	655
J	-	1123	2165	-	2545	565
K	-	1295	2515	-	2800	525
L	-	872	1640	-	1950	570
M	-	881	1820	-	2140	575

Stock	Cure	Modulus at			Tensile @ Break	Ult. Elong.
		300%	500%	700%		
A	120′/20 lbs.	1950	3900	-	4775	585
B	-	2095	4235	-	4780	545
C	-	1750	3615	-	4380	600
D	-	1910	3870	-	4290	570
E	-	1525	3070	-	3595	565
F	-	1820	3325	-	3490	530
G	-	1465	2795	-	3160	580
H	-	1695	3155	-	3215	515
J	-	1330	2425	-	2620	545
K	-	1540	-	-	2795	490
L	-	1000	1860	-	2020	540
M	-	1125	2080	-	2150	515
A	180′/20 lbs.	2035	4030	-	4370	535
B	-	2120	4240	-	4445	520
C	-	1825	3710	-	4005	540
D	-	2035	3870	-	4200	535
E	-	1490	3070	-	3675	575
F	-	1720	3145	-	3215	515
G	-	1400	2875	-	3115	530
H	-	1565	2935	-	3140	525
J	-	1350	2475	-	2595	525
K	-	1475	2715	-	2715	500
L	-	1115	2030	-	2165	520
M	-	1235	-	-	2180	495
A	30′/30 lbs.	1188	2750	4495	4495	700
B	-	1360	3145	-	4725	665
C	-	1095	2635	4355	4355	700
D	-	1265	2900	-	4325	685
E	-	996	2315	-	3250	640
F	-	1305	2650	-	3275	605
G	-	1005	2240	-	3000	630
H	-	1144	2440	-	3210	615
J	-	1090	1325	-	1960	645
K	-	1113	2185	-	2660	580
L	-	728	1415	-	1760	615
M	-	796	1585	-	1975	600

Stock	Cure	Modulus at			Tensile	Ult.
		300%	500%	700%	@ Break	Elong.
A	60′/30 lbs.	1660	3570	-	4660	620
B	-	1950	3905	-	4455	545
C	-	1580	3530	-	4515	630
D	-	1745	3630	-	4450	610
E	-	1475	2930	-	3570	600
F	-	1685	3160	-	3200	510
G	-	1470	2770	-	3145	560
H	-	1580	2940	-	3105	515
J	-	1310	2420	-	2535	530
K	-	1565	2690	-	2690	500
L	-	971	1820	-	1985	535
M	-	1055	1960	-	2170	540
A	90′/30 lbs.	1835	3750	-	4655	590
B	-	2030	3900	-	4525	530
C	-	1715	3570	-	4260	590
D	-	1835	3890	-	4110	540
E	-	1428	2895	-	3450	535
F	-	1585	3070	-	3165	510
G	-	1400	2780	-	2980	525
H	-	1505	2895	-	3050	510
J	-	1260	2355	-	2510	515
K	-	1435	2625	-	2625	500
L	-	1070	2050	-	2050	500
M	-	1150	2155	-	2175	505
A	120′/30 lbs.	1860	3825	-	4335	560
B	-	2025	3985	-	4485	545
C	-	1780	3630	-	4230	580
D	-	1750	3630	-	3880	535
E	-	1385	2805	-	3420	580
F	-	1685	-	-	3055	495
G	-	1360	2670	-	2740	510
H	-	1480	2905	-	2905	500
J	-	1240	2365	-	2365	500
K	-	1330	-	-	2460	485
L	-	1110	2005	-	2005	500
M	-	1165	2115	-	2116	510

The above figures show the gradual reduction in tensile strength which takes place with increasing quantities of reclaim substituted for raw rubber. Likewise, the elongation becomes progressively shortened as more and more reclaim is present. The modulus is similarly reduced.

Carcass Stocks.

Similar figures to the above are now shown illustrating the effect of increasing amounts of reclaim in *Ureka* carcass stocks:—

	A	B	C	D	E	F	G	H
Smoked sheets ..	40	40	50	50	35	35	20	20
Softer Rubber ..	25	25	-	-	-	-	-	-
Whole tyre reclaim	10	10	28	28	43	43	50	50
Tube or carcass reclaim	10	10	7	7	10	10	18	18
Zinc Oxide ..	7	7	5.5	5.5	4	4	4	4
Stearic acid ..	0.6	0.6	0.5	0.5	-	-	-	-
Tackol	2	2	2	2	2	2	2	2
Sulphur	2.85	2.85	2.65	2.65	2.5	2.5	2.25	2.25
Ureka	0.5	0.6	0.5	0.6	0.5	0.65	0.45	0.55

Stock	**Cure**	**Modulus at** 300%	500%	700%	**Tensile @ Break**	**Ult. Elong.**
A	30′/20 lbs.	207	523	1725	2290	780
B	-	245	650	2125	3170	805
C	-	220	560	1640	2425	810
D	-	280	720	2085	2985	800
E	-	281	766	1925	1925	700
F	-	390	998	2600	2765	710
G	-	315	722	1545	1545	700
H	-	332	767	-	1670	690

Stock	**Cure**	**Modulus at**			**Tensile**	**Ult.**
		300%	500%	700%	**@ Break**	**Elong.**
A	60′/20 lbs.	348	929	2955	3370	725
B	-	404	1170	3500	3905	735
C	-	391	1020	2775	3135	735
D	-	418	1200	3300	3560	720
E	-	439	1205	-	2590	685
F	-	638	1665	-	2950	655
G	-	469	1115	-	2025	665
H	-	525	1285	-	2120	650
A	90′/20 lbs.	380	1130	3465	3710	710
B	-	435	1365	3990	3990	700
C	-	435	1315	3375	3375	700
D	-	498	1530	3660	3660	700
E	-	538	1570	-	2600	635
F	-	703	1795	-	2635	610
G	-	570	1345	-	2140	615
H	-	613	1530	-	2210	605
A	120′/20 lbs.	433	1240	-	3600	695
B	-	515	1510	-	3910	690
C	-	495	1405	-	3370	680
D	-	565	1620	-	3330	650
E	-	613	1680	-	2755	630
F	-	735	1930	-	2795	605
G	-	648	1575	-	2045	590
H	-	745	1750	-	2170	560
A	180′/20 lbs.	476	1385	-	3570	685
B	-	533	1575	-	3645	675
C	-	558	1620	-	3250	660
D	-	627	1870	-	3190	630
E	-	659	1750	-	2610	605
F	-	799	2075	-	2610	570
G	-	727	1680	-	1820	515
H	-	775	1835	-	1985	525

Stock	**Cure**	**Modulus at**			**Tensile**	**Ult.**
		300%	500%	700%	**@ Break**	**Elong.**
A	30′/30 lbs.	329	1000	3025	3210	715
B	-	386	1163	3385	3775	735
C	-	391	1187	3130	3180	710
D	-	451	1297	-	3320	695
E	-	456	1180	-	2410	675
F	-	535	1485	-	2590	625
G	-	474	1130	-	1885	635
H	-	500	1245	-	2095	635
A	60′/30 lbs.	445	1335	-	3710	695
B	-	497	1500	-	3880	690
C	-	494	1570	-	3325	690
D	-	556	1630	-	3530	665
E	-	616	1625	-	2620	620
F	-	704	1880	-	2625	585
G	-	621	1505	-	2030	575
H	-	641	1640	-	2040	535
A	90′/30 lbs.	449	1280	-	3335	665
B	-	490	1382	-	3545	665
C	-	530	1530	-	3165	650
D	-	578	1820	-	3180	630
E	-	672	1745	-	2450	585
F	-	756	2105	-	2505	545
G	-	686	1635	-	1930	550
H	-	660	1632	-	1920	535
A	120′/30 lbs.	442	1255	-	3240	675
B	-	500	1515	-	3615	670
C	-	546	1575	-	2990	615
D	-	596	1725	-	3025	620
E	-	634	1645	-	2255	570
F	-	727	1870	-	2275	550
G	-	689	1600	-	1770	510
H	-	659	1590	-	1695	545

A study of the above figures shows that the same general reduction in tensile strength and other properties is brought about when raw rubber is replaced by reclaim. Whilst the initial cure, evidenced by the 30 minutes cures shown, is very little changed from the point of view of activity, the stocks with increasing reclaim do not stand overcure so well, and the ultimate elongation is considerably reduced.

All the figures shown above illustrate the effect of increasing reclaim contents in a stock accelerated only with *Ureka.* The following series show the effect of increasing reclaim contents with other accelerators, such as *Ureka HR*, *A-16*, and *Thiotax.*

S. 208		A	B	C	D
Smoked sheets	....	34	34	34	34
Whole Tyre Reclaim	....	34	34	34	34
Mineral Rubber	....	3	3	3	3
Tackol	....	2	2	2	2
Zinc Oxide	....	4	4	4	4
Carbon Black	....	21	21	21	21
Sulphur	....	1.85	1.85	1.85	1.85
Thiotax	....	0.60	0.75	-	-
A-16	....	-	-	0.60	0.75

Cures: 10, 20, 30, 45 and 60 minutes at 40 lbs.

Cure	Stock	Modulus at 200%	300%	500%	Tensile @Break	Ult. Elong.
10′/40 lbs.	S. 208 A	723	1233	2495	2785	560
	B	790	1383	2645	2890	550
	C	372	700	1525	1880	585
	D	420	795	1770	2175	585
20′/40 lbs.	S. 208 A	870	1475	2765	2810	515
	B	925	1610	2870	2870	500
	C	530	970	2020	2530	605
	D	600	1098	2290	2780	600

Cure	**Stock**	**Modulus at**			**Tensile**	**Ult.**
		200%	300%	500%	**@Break**	**Elong.**
30′/40 lbs.	S. 208 A	860	1485	2700	2720	505
	B	925	1570	-	2800	490
	C	595	1125	2240	2685	590
	D	680	1230	2530	2840	550
45′/40 lbs.	S. 208 A	835	1430	2620	2620	500
	B	845	1430	-	2650	485
	C	705	1290	2395	2755	565
	D	768	1350	2620	2795	530
60′/40 lbr.	S. 208 A	785	1335	-	2485	495
	B	830	1400	-	2480	480
	C	760	1300	2450	2725	555
	D	763	1390	2635	2795	530

S. 209	A	B	C	D
Smoked sheets	12	12	12	12
Whole Tyre Reclaim	75	75	75	75
Mineral Rubber	3	3	3	3
Tackol ...	3	3	3	3
Zinc Oxide	4	4	4	4
Sulphur	2.00	2.00	2.00	2.00
Thiotax	0.45	0.55	-	-
A-16	-	-	0.45	0.55

Cures: 10, 20, 30, 45, and 60 minutes at 35 lbs.

Cure	**Stock**	**Modulus at**			**Tensile**	**Ult.**
		200%	300%	500%	**@Break**	**Elong.**
10′/35 lbs.	S. 209 A	366	631	1380	1600	540
	B	373	600	1315	1360	510
	C	216	365	-	505	385
	D	237	405	900	1040	540

Cure	**Stock**	**Modulus at**			**Tensile**	**Ult.**
		200%	300%	500%	@**Break**	**Elong.**
20′/35 lbs.	S. 209 A	477	805	-	1520	470
	B	485	795	-	1600	480
	C	322	535	1185	1325	535
	D	342	570	1290	1445	540
30′/35 lbs.	S. 209 A	488	830	-	1425	440
	B	495	833	-	1410	440
	C	365	600	1370	1420	520
	D	377	660	1445	1445	500
45′/35 S. lbs.	209 A	503	845	-	1173	380
	B	480	823	-	1385	435
	C	375	635	1360	1360	500
	D	412	693	1490	1490	500
60′/35 lbs	S. 209 A	473	790	-	1030	365
	B	470	785	-	1245	415
	C	392	665	-	1360	485
	D	382	655	-	1345	485

The above stocks illustrate the behaviour of *Thiotax* and *A-16*, both in a tread stock containing an equal quantity of reclaim and new rubber, and in a carcass stock compounded to contain about the maximum permissible quantity of reclaim consistent with easy handling in the factory. It will be noticed that Thiotax gives a very fast curing stock which is scorchy and, therefore, very susceptible to differences which may exist during processing of the stocks in the factory. The A-16 stocks, however, come up to the proper cure in sufficient time to make them suitable for the present-day cures, and yet are considerably safer to handle.

The same remarks apply equally to the carcass stock, and it should be particularly noted that the A-16 stocks do not overcure as rapidly with this high concentration of reclaim present as those containing Thiotax. As previously mentioned, A-16 is an excellent accelerator for use with reclaim tread stocks. Suggestions as to the use of Ureka HR and A-16 for mechanical stocks are given below:—

S. 208	E	F	G	H
Smoked sheets	34	34	34	34
Whole Tyre Reclaim	34	34	34	34
Carbon Black	20	20	20	20
Zinc oxide	4	4	4	4
Stearic acid	0.5	0.5	0.5	0.5
Tackol	1	1	1	1
Mineral Rubber	2	2	2	2
Sulphur	1.6	1.6	1.6	1.6
Thiotax	0.40	0.60	-	-
Ureka HR	-	-	0.40	0.60

Cures: 20, 30, 45, 60 and 90 minutes at 30 lbs.

Cure	**Stock**	**Modulus at** 200%	300%	500%	**Tensile @ Break**	**Ult. Elong.**
20′/30 lbs.	S. 208 E	618	1130	2385	3065	610
	F	750	1375	2750	3355	590
	G	442	818	1855	2780	655
	H	690	1290	2640	3280	615
30′/30 lbs.	S. 208 E	715	1310	2600	3150	600
	F	825	1483	2860	3340	570
	G	528	1005	2200	2940	620
	H	805	1460	2940	3345	570
45′/30 lbs.	S. 208 E	753	1313	2650	3025	570
	F	815	1460	2860	3260	560
	G	635	1190	2460	3150	610
	H	883	1595	3040	3370	535

Cure	**Stock**	**Modulus at** 200%	300%	500%	**Tensile** @ **Break**	**Ult. Elong.**
60′/30 lbs.	S. 208 E	730	1298	2590	3020	570
	F	790	1390	2770	3120	550
	G	708	1240	2570	3130	585
	H	908	1640	3165	3265	515
90′/30 lbs.	S. 208 E	665	1208	2470	2790	560
	F	715	1290	2660	3020	560
	G	745	1340	2640	3060	565
	H	893	1580	3070	3200	620

The E, F, G, and H series show a comparison between Thiotax and Ureka HR in a reclaim tread stock. The Thiotax stocks again seem to be very fast curing but liable to overcure rather quickly. Ureka HR is a little faster than A-16 in reclaim stocks but is safer than Thiotax. Further, the figures illustrate that the Ureka HR will stand overcure somewhat better than Thiotax.

Finally, we show below a further series of four stocks using Ureka HR as accelerator, and introducing varying quantities of whole tyre reclaim. This series will illustrate what can be expected of a stock when fresh rubber is substituted by reclaim:

C. 317	A	B	C	D
Smoked sheets	50	45	40	35
Whole Tyre reclaim	-	10	20	30
Zinc oxide	4	4	4	4
Carbon black	21	20	19	18
Stearic acid ...	1	1	1	1
Tackol	2	1	1	1
Mineral Rubber	-	2	2	2
Sulphur	1.4	1.5	1.55	1.6
Ureka HR	0.6	0.6	0.55	0.5

Cures: 20, 30, 45, 60 and 90 minutes at 30 lbs.

Cure	**Stock**		**Modulus at**			**Tensile**	**Ult.**
			200%	300%	500%	**@ Break**	**Elong.**
20′/30 lbs.	C. 317	A	230	509	1398	2075	635
		B	499	933	2280	3685	680
		C	589	1125	2430	3820	690
		D	498	939	2095	3135	670
30′/30 lbs.	C. 317	A	659	1298	2885	4315	660
		B	806	1530	3170	4075	610
		C	865	1508	3075	3960	610
		D	736	1340	2735	3510	610
45′/30 lbs.	C. 317	A	739	1445	3135	4405	640
		B	887	1610	3350	4070	565
		C	875	1600	3140	3970	595
		D	762	1388	2830	3520	600
60′/30 lbs.	C. 317	A	803	1515	3240	4300	615
		B	888	1585	3330	3970	550
		C	915	1613	3205	3920	585
		D	783	1383	2850	3525	585
90′/30 lbs.	C. 317	A	871	1645	3455	4125	578
		B	872	1625	3325	3870	555
		C	873	1618	3135	3350	530
		D	815	1443	2885	3295	560

In none of the stocks shown in this chapter have anti-oxidants been introduced. Whilst the presence of an anti-oxidant in relaimed rubber stocks is not only desirable, but of considerable value, it was considered to be of more use for these stocks to contain as few variable factors as possible.

Hereafter are a few formulas for different stocks with reclaim:—

Heel Stock.

	Black	*Tan*
Smoked sheets	10^{k}	12^{k}
Whole Tyre reclaim	56^{k}	-
Tube reclaim	-	36^{k}
Mineral rubber	3^{k}	3^{k}
Zinc oxide	5^{k}	8^{k}
Carbon black	6^{k}	-
Red iron oxide	-	2^{k}
Kaolin	16^{k} 5	30^{k}
Stearic acid	0^{k} 5	0^{k} 5
Sulphur	1^{k} 5	1^{k} 5
A-16	0^{k} 5	0^{k} 4

Cure: 12 minutes at 65 lbs.

Sole Stock.

	Black	*Tan*
Smoked sheets	16^{k}	25^{k}
Whole Tyre reclaim	44^{k}	-
Mineral rubber	-	6^{k} 5
Zinc oxide	3^{k} 9	16^{k}
Carbon black	31^{k}	-
Mag. Carbonate	-	27^{k}
Kaolin	-	10^{k}
Blanc Fixe	-	8^{k}
Red iron oxide	-	4^{k}
Tackol	2^{k}	0^{k} 25
Stearic acid	0^{k} 5	1^{k}
Sulphur	1^{k} 6	1^{k} 25
A-16	0^{k} 6	0^{k} 45

Cure: 18 minutes at 60 lbs.

Cheap Articles made wholly from Reclaim.

Rubber	5^k
Whole Tyre reclaim	60^k
Zinc oxide	2^k
Whiting	30^k
China clay	10^k
Mineral rubber	5^k
Stearic acid	0^k 25
Tackol	0^k 5
Sulphur	1^k 3
A-32	0^k 3

Cure in steam: 10 minutes at 40 lbs. or higher.

Hose.

	Inner and Outer layer	*For Solution or Friction*
Smoked sheets	32^k	16^k
Tube reclaim	-	25^k
Whiting	-	15^k
Softer rubber	-	15^k
Mineral rubber	-	4^k
Whole Tyre reclaim	20^k	-
Carbon black	7^k 5	-
China clay	22^k 75	-
Asbestine	15^k	-
Zinc oxide	10^k	20^k
Stearic acid	0^k 5	0^k 5
Sulphur	1^k 625	2^k 25
A-16	0^k 20	0^k 45
A-510	0_k 45	-

Cure in open steam: 50 minutes at 40 lbs.

Ureka HR Tyres.

	Tread	*Carcass*
Smoked sheets	40^{k}	-
Softer rubber	-	40^{k}
Whole Tyre reclaim	10^{k}	40^{k}
Carbon black	20^{k}	-
Mineral rubber	3^{k}	10^{k} 5
Soft black	-	16^{k}
Zinc oxide	5^{k}	3^{k}
Stearic acid	1^{k}	0^{k} 75
Tackol	1^{k}	-
Sulphur	1^{k} 6	2^{k} 2
Ureka HR	0^{k} 55	0^{k} 625
Flectol B	0^{k} 4	0^{k} 4

Cure in Watch-Case: 10 mins. at 25 lbs. steam pressure.

A-11 Tread.

	Tread	*Carcass*
Smoked sheets	40^{k}	35^{k}
Whole Tyre reclaim	27^{k}	30^{k}
Carbon black	20^{k}	-
Mineral rubber	5^{k}	5^{k}
Zinc oxide	6^{k}	15^{k}
Stearic acid	1^{k}	1^{k}
Tackol	1^{k}	-
Sulphur	2^{k} 25	2^{k}
A-11	0^{k} 875	0^{k} 5
Flectol B	0^{k} 3	0^{k} 3

Cure in Watch-Case: 10 mins. at 35 lbs. steam pressure.

CHAPTER VIII.

The Moulding of Rubber Goods.

THE moulding of a plastic material to fill perfectly all cavities in a mould is not always as easily done as it would seem. In the rubber industry the moulding of the plastic mass and its vulcanisation is accomplished more or less simultaneously, in so far as the manual operations are concerned. It is necessary, however, that the flow of stock in the mould be complete before vulcanisation actually sets in.

The chief consideration is to have the rubber stock fill perfectly all portions of the mould. Very frequently this is a fairly difficult task and is often a source of considerable trouble in the Works. There are a large number of reasons why the stocks will not flow and properly fill all cavities, but when these reasons are explained they appear relatively simple.

The first thing that must be realized is that initially the mould is full of air, and before the rubber can take the place occupied by this air, the air itself must have some way of escape. If the air is trapped in a corner of the mould, it merely becomes compressed to a high degree, and when the back pressure caused by this compression, equals that imposed by the hydraulic ram, no further flow of stock will take place. The rubber articles will then have their corners rounded instead of having sharp, square lines as was intended. Air may be trapped not only in certain corners of the mould, but along flat surfaces and along edges. It must be remembered, that as the rubber is placed in a hot mould it softens rather readily. This soft rubber on being squeezed by the hydraulic pressure, makes a very perfect gas-tight seal and usually prevents air from escaping. In order to overcome this, the shape of the article placed in the mould must be such that the rubber will tend to fill the remote cavities of the mould before squeezing over and closing up the overflow. Thus, for example, if we were to mould a cube and wanted to fill perfectly the eight corners of the cube, we would not necessarily try to place a stock cut cubical in shape in the mould. If we place in the mould a piece of rubber almost spherical in shape, we will see as soon as the mould closes contact is first made in the centre of each face and as the mould is gradually tightened the edges flatten out with the result that the stock gradually flows into each corner of the cube. If no provisions were made for the escape of the air in these corners, the cube would probably be vulcanised with each corner rounded, but if we provide a vent hole in each corner then the stock would flow perfectly and fill to form sharp, pointed corners. Ordinarily, a mould of this character will come apart along four of these corners, and as the mould itself does not make an air tight fit, the escape of air at these four corners would be more or less automatic.

If instead of using a spherical piece of rubber we put in a piece more in the shape of a truncated pyramid, we would find that the bottom four corners would fill out immediately the hydraulic pressure was applied and the flow of the stock would gradually push all the remaining air up and out through the mould opening at the top. This would be an improvement in the original shape, in case our mould had the usual opening at the top. Theoretically, a still better shape to be placed in the mould would be more in the shape of a cube on the bottom but growing slightly smaller as it approaches the top and well rounded at the top edge. This piece would, of course, be a little higher than the opening in the mould to provide sufficient stock to completely fill it. Now, when the pressure squeezes the top and bottom half together, it will be seen that the mould will fill perfectly, first from the bottom and then the line of contact will gradually move up on all sides to the top and no air will be trapped in any place.

The same basic principles illustrated here must be used in shaping all raw stock for moulding. Generally, of course, raw stock is shaped as much like the shape of the finished article as possible, with the exception that where this shape does cause air to be trapped, certain modifications must then be made. Stock must also be of a shape easy to manufacture, such as extruded or calendered pieces, or punchings from sheets.

Frequently, certain mould designs are such, that it is more or less impossible to shape the article originally so as to prevent the trapping of air in certain portions of the mould. When this is the case, small vents are often cut from one portion of the mould to another, to permit the air to travel always from the remote portions of the mould to the centre or opening line. An excellent example of this type of moulding is to be observed in the non-skid pattern of the ordinary motor car tyre. In the regular designs, the edges of the non-skids are connected up by small vent cleavages. to the irregularity near the centre line so that the air may escape through these cleavages to the centre of the mould and out through the overflow.

Frequently, it is impossible to accomplish either of the foregoing and then the remedy is to drill holes from the inside to the outside of the mould. This should be done only as a last resort as trouble is frequently encountered owing to these holes becoming plugged up with the stock. This method is usually only satisfactory in the case of high grade stocks, where rubber is relatively tough and will pull out cleanly from these holes.

It will be noted that the opening of the mould is usually depended upon to take away most of the air. Normally, the mould opens in the middle or on the flat top or bottom surface. Frequently this mould opening should be altered to some other point, where the air can escape more readily. At other times, the same thing is accomplished by providing a vent hole from this region of the mould to a centre or top or bottom opening.

It is frequently found that freshly run stock will not mould properly, but will trap air badly. This same stock, if permitted to lie around two or three days, works perfectly. The explanation is merely that the fresh stock being soft and sticky, adheres to the mould readily, and thus traps air badly. After some time it is somewhat stiffer and has lost its tacky surface, probably because of both blooming and air drying. It no longer sticks to the mould so readily, and consequently air escapes easily. As a result, the stock now moulds perfectly.

It is obvious that in case there is insufficient stock to fill a mould completely, the stock will ordinarily vulcanise in a rather spongy condition. One frequently finds this the case where there is some overflow, and yet a spongy condition in the cured stock. This usually means that the shape of the unvulcanised article was not suitable and that the quick application of high hydraulic pressure caused an overflow before the bulk of the stock had time to flow to its ultimate location. After the stock had flowed there was insufficient material to fill the mould completely, even though the overflow was made during the process.

It often happens, when dealing with stock that vulcanises quite rapidly that a slight vulcanisation will take place before the stock has had time to flow properly. When this happens, the mould ordinarily never fills up completely, and all edges are more or less rounded instead of being clean and sharp. The same results are obtained when the stock is too stiff to flow properly, or the hydraulic pressure is insufficient to cause it to flow. In the manufacture of a mould for rubber work, a good deal of thought must usually be given to the design of the overflow cavities. If they are too small to accommodate the overflow of stock, they plug up and seal the mould air-tight, and thus cause trapped-air trouble referred to previously. On the other hand, they can be too large and permit the stock to flow out too readily, giving insufficient resistance or back pressure to fill the mould properly. These overflow cavities are placed on the division of the mould so as to permit the air to escape through them.

To produce smooth articles, moulds must be kept clean and polished. For exceptionally smooth articles, the moulds should be tinned inside, Chromium plating is also being used to a certain extent in view of obtaining very smooth articles. Moulds may be cleaned by several methods. Generally after each cure they are brushed with an ordinary brush; in some Works wire brushes are used, but this practice is not recommended for highly polished or delicate moulds as it causes the surface to be scratched badly. After continued use for some time, there is in a varying degree an accumulation of rubber, talc and solution on the mould, particularly in the crevices that are hard to reach with an ordinary brush. This may be removed by a burning or treating with chemicals. Large moulds are usually "burned". This operation consists of moving an oxy-acetylene-flame over the surface of the mould. This flame is very hot and if permitted to stand, will melt the mould! An experienced operator is required for this work, one who has learned that if he does not keep his flame moving, he will ruin the mould, but that if he keeps it moving too rapidly, he will not burn out the accumulation of dirt. All that is required is a temperature just sufficient to char and loosen any accumulation of organic matter in the moulds. While this practice sounds rather risky, it is extensively employed as the most economical method of cleaning large moulds. The heat will cause the accumulation of organic matter to swell up and loosen from the mould, and it can then be readily brushed off with an ordinary brush. Moulds have frequently been cleansed by immersion in bath of molten lead, which likewise causes the organic matter to char and thus be removed easily. Similarly, moulds have been treated by boiling in caustic solution and afterwards brushed in the ordinary manner. This last treatment is perhaps more common with small moulds, while the oxy-acetylene-flame is more commonly used for the large ones.

The ordinary specifications for the cure of rubber goods call for holding a certain definite temperature for a definite period of time. Ordinarily, this temperature is expressed as that equivalent to so many pounds of steam pressure, though modern practice tends to get away from this steam pressure nomenclature and to express temperature, as it properly should be expressed, in degrees Fahrenheit or Centigrade. Pressure alone does not vulcanise rubber and it is only the temperature that can accomplish this. Steam gauges, unfortunately, indicate pressure only, and this pressure may be partially due to trapped air and thus give us inaccurate indications of our temperature. In order that press cured articles may be heated to a proper degree, the press platens must be maintained at the full temperature designated. To accomplish this all condensation must be easily drained from within the platens. Only too often platens of two or three inches in thickness are manufactured with a small exhaust pipe in the centre, which permits a layer of condensation to lay on the bottom part of the steam chamber. In such cases either the outlet hole must be enlarged, or the press inclined slightly so that the water will drain out. In multiple opening presses it is much better to manifold the steam rather than to have it run from platen to platen in series. A most common source of trouble for temperature control is the existence of air mixed with the steam supply. This causes trouble, particularly in individual tyre and tube mould work, while air already in the vulcaniser and that escaping from air lines also cause difficulties in open steam heaters and hydraulic type tyre vulcanisers.

Water, from which steam is generated, unfortunately, always contains a small quantity of dissolved air. This passes along with the steam into the cavity of the presses. Here the water vapour condenses and is exhausted either through a steam trap or temperature condensation control. No provision is ordinarily made to let out this accumulation of air which gradually builds up a greater and increasing concentration. This frequently pockets in the inaccessiable corners of the platens that are removed from the main stream of steam. Consequently, the temperature here is lower, although the pressure is, of course, uniform. It is necessary that all installations of this character be designed to bleed out a certain small quantity of steam which will take with it the accumulated air. Usually, a recording thermometer is attached to the press, and this instrument may be attached in such a way as to demand a small current of steam passing through the coupling. If no such outlet is provided, a small petcock should be attached to each press platen or cavity and permitted to allow a very small stream of steam to escape continuously. It frequently happens that in older Works in which the vulcanising presses are in bad condition and leak in a number of places, good work is obtained and that when these presses are properly repaired and made steam-tight, poor cures result. This is very easily explained by the trapping of air resulting from tight joints. If moulds are placed in an open steam heater and the latter then filled with steam, the air originally contained therein must be allowed to escape or it will settle to the bottom of the heater, and cure here will not be satisfactory. Ordinarily, steam is turned into the top or side of the vulcaniser and the drain left open for a minute or so, or until steam is flowing quite freely from it. It is then closed and the steam pressure permitted to build up in the vulcaniser.

Fortunately, more and more use of automatic temperature control is being made in the industry. Such equipment will normally guarantee the proper temperature in the steam cavity. Its use eliminates at least one variable, namely, that of loss of temperature due to air pressure. With this equipment, air will not bother us except that we must not let it pocket in any place.

In the moulding of tyres, where the moulds are stacked in a vertical vulcaniser, air not only is introduced with the steam but frequently is present in increased amounts on account of leaks from the lines to the air bags. Usually there are two or more recording or controlling instruments attached to the vulcaniser, which draw off a small quantity of steam, but in case of a leak in the air bag line, this is insufficient to remove the air content. Fortunately, practically all tyre heaters are now controlled by automatic temperature regulators, which means that no attention is paid to the pressure present. It becomes necessary then not to see that the air is released from the vulcaniser, but merely to see that it is uniformly distributed and mixed with the steam so that no local under-curing may occur because of pockets of air preventing the steam from reaching any particular portion of the vulcaniser. One method of doing this is to cause the contents of the vulcaniser to circulate by means of an injector placed on the inlet steam line. This injector is operated by the usual passage of inlet steam and draws steam from some remote portions or opposite sections of the vulcaniser, thereby setting up a circulation. In other systems the inlet steam is introduced under high pressure and through a small opening in the form of nozzle, so placed as to cause a continuous swirl or agitation of the contents of the vulcaniser. Such methods as these prevent air pockets and permit uniform temperature conditions. These conditions are obtained even though there may be a total pressure of 45 or 50 lbs. per square inch in the vulcaniser but a temperature of only 286° or 288° F.

As an indication, the following are Steam Pressure and Temperatue Comparisons:

Gauge Pressures (above atmospheric)			**Temperature**	
lbs. 1 sq. in.	kg/cm²	Atmospheres	°C	°F
0	0.00	0.00	100	212
5	.35	.34	109	227
10	.70	.68	115	239
15	1.05	1.02	121	250
20	1.41	1.36	125	258

Gauge Pressures (above atmospheric)			**Temperature**	
lbs. 1 sq. in.	kg/cm^2	Atmospheres	°C	°F
22	1.55	1.50	127	261
24	1.69	1.63	129	265
26	1.83	1.77	131	268
28	1.97	1.90	133	271
30	2.11	2.04	134	274
32	2.25	2.18	136	277
34	2.39	2.31	138	280
36	2.53	2.45	139	282
38	2.67	2.58	140	285
40	2.81	2.72	141	287
42	2.95	2.86	143	290
44	3.09	2.99	144	292
46	3.23	3.13	145	294
48	3.37	3.26	147	296
50	3.52	3.40	148	298
52	3.66	3.54	149	300
54	3.80	3.67	150	302
56	3.94	3.81	151	304
58	4.08	3.94	152	305
60	4.22	4.08	153	307
65	4.57	4.42	155	312
70	4.92	4.76	158	316
75	5.27	5.10	160	320
80	5.62	5.44	162	324
85	5.98	5.78	164	327
90	6.33	6.12	166	330
95	6.68	6.46	168	334
100	7.03	6.80	170	337
110	7.73	7.48	173	344
120	8.44	8.16	177	350

If we again consider press cured goods, we realise that the moulds are removed from the presses for a certain period while the articles are being taken out and replaced by others. In some cases, this time outside of the press is relatively long and permits the moulds to cool off considerably. We must take into consideration particularly, any difference in this length of time as any non-uniformity here will cause considerable variation in the final cure obtained. Since the heat received by the mould must be transferred by metallic contact from the press platen to the mould, it is essential that both be perfectly flat and clean. A layer of rust on either will materially lengthen the time of cure. In case either surface is warped considerably, a layer of air is introduced between the two and the transfer of heat is materially retarded. Moulds must not be placed too near the edge of the platen on account of too great air cooling caused by this exposure. This can be partially remedied by building an insulating screen round two or three sides of the press. Unfortunately, it is rather difficult to enclose the press completely with insulation without it being rather cumbersome; usually one side must remain open continually and frequently two sides of the press. It is not unusual to find that articles bloom heavily when vulcanised near the edge of the press platen but remain strictly non-blooming when vulcanised near the centre.

Such conditions as these just mentioned cause this irregularity as well as a variation in results obtained from one platen to another and from one mould to another. It is often found that the press platens are badly warped by some operator using full hydraulic pressure when only a small single mould was placed in the centre of the press.

In spite of the relatively high polish given to some moulds, it may be taken as an accepted fact that all moulds have more or less rough surfaces. This is especially apparent if the surface is observed under a microscope. When the rubber stock is softened by the heat and then placed under a very high pressure, the tendency is for it to press into these microscopic pores on the mould surface. Obviously, the softer the stock, the more easily it should flow. It is found in practice that rubber, both vulcanised and unvulcanised sticks quite readily to metal surfaces. If the rubber is soft and unvulcanised, it sticks quite badly, the situation here being essentially the same as with a friction stock on a good hot calender roll. The tougher and drier the stock, the less the tendency to stick. The higher the state of vulcanisation, the less the sticking.

On removing a rubber article hot from a hot mould, it will be frequently found that the rubber article cracks, where much strain is placed on it. It is rather common knowledge that rubber at vulcanisation temperatures is degraded considerably in its physical properties. The metallurgical term *hot short*, meaning somewhat brittle when hot, can well be applied here. Nevertheless, some intricate designs necessitate relatively severe strains on the rubber during the removal from the mould. Sometimes, it is necessary to cool the mould partially to avoid damage, but frequently if the moulds are cooled too much, the power necessary to distort the rubber sufficiently to get it out of the mould becomes so great that the task of removing the article is made a very difficult one. These remarks apply particularly to motor car tyres as well as to ordinary press cured moulded goods. While the usual mould is a two piece one, frequently three or four piece moulds are made to overcome this difficulty of removing the article from the mould.

Obviously, if a film of some material that could be maintained liquid was placed between the rubber and the mould, little or no difficulty would be encountered in the removal of the article. This film would have to be microscopically thin to prevent accumulation on the mould or sticking to the article itself. Monsanto, as far as we know, have made a *mould paste* which, if properly used, will supply this film. Any mould solution or mould dope to work satisfactorily must give this thin greasy film between the rubber and the mould. The thinner the film that can be obtained without breaking, the more satisfactory the solution. This film must not be dissolved by the rubber; must not corrode the mould; must also have other properties so that it will not accumulate in the mould, and preferably should not discolour white or light coloured articles. The best way of applying such a solution is by a compressed air spray nozzle and the solution should not gum up the nozzle.

The film produced by the mould solution must not be destroyed by the temperature of the mould and must also stick sufficiently to the mould so as not to be wiped off completely by the movement or flow of the rubber stock during the compression period. The Monsanto Mould Paste meets this requirement. It is said to be a composition of several materials so blended that this mixture will hold, at the usual vulcanizing temperature, just sufficient moisture to make a coating of the proper consistency even though the mould is quite hot and the solution is applied in the form of a very thin one. The excess water will be evaporated until the concentration of the solution is just right for the moulding operation. This film then prevents the rubber from coming in contact with the mould and thereby permits of its easy removal.

The Mould Paste is usually packed in individual containers of 10 lbs. each, and the entire contents of a tin should be dissolved in water at one time. The mixture in this 10 lb. tin is not necessarily homogeneous, and requires therefore complete solution of the contents. A concentrated solution may be made and this may be dissolved later as required. Ordinarily, the contents of a 10 lb. tin (approximately 1 gallon) are diluted with from 30 to 50 gallons of water. This solution is brushed or sprayed on the mould every two or three heats or when the stock shows signs of sticking. With new moulds or one just cleaned, the solution should be applied after each heat for the first few cures.

We get quickly accustomed to the use of this solution, and realise, when articles show a tendency to stick, that we should use the paste a little more frequently or spray a little more of it. On the other hand, if too much of the solution is used, the article will have a sticky, greasy feeling after removal from the mould. The best results are obtained by using a minimum amount of solution. The Monsanto mould solution can also be applied directly to press plates in the vulcanization of belting, and so forth. Here the solution is not made quite as thin, but is applied less frequently, and it has been found that the said mould solution can also be used for the treatment of cloth wrappings used to cover hose, inner tubes and the like, and prevents the cloth from sticking to the rubber. It is also used as a solution in which to dip air bags to prevent their sticking to the inside of the tyre. In short, it may be used on almost any other material coming in contact with rubber, where it is desired that the rubber should not stick to the other article.

CHAPTER IX.

The Laboratory.

WHAT has been said in chapters VII and VIII of this publication is the result of correspondence exchanged between the author and the Monsanto Chemical Works Ltd., whose notes were of much help in the preparation of the foregone pages.

The Monsanto Chemical Works, desirous of helping the Rubber Manufacturer, have established a laboratory as detailed hereunder, and the illustrations given hereafter are reproductions of photographs, which they sent, of some of their Testing Machines. The establishment of this laboratory was found necessary for the reason that the working of rubber has up to recent years been much more of an art than a science, whereas now-a-days the combined efforts of Chemists, Physicists and practical workmen have gradually introduced more and more science into the manufacture of rubber goods; and Monsanto are of opinion that it is the duty of the manufacturer of materials for rubber Works to go extensively into investigation and development of his products, if they are to be of value to the industry.

So, a manufacturer of chemicals must understand thoroughly all major operations in rubber goods manufacture and be familiar not only with the general procedure, but with all the important details as well. He must know the chemistry, the mechanics and the works details of everything that goes on in the factory.

Yet, the rubber industry is still young, but it is growing rapidly and changes are being made in many directions. Old processes are being discarded for newer and better ones. Old equipment is being scrapped for

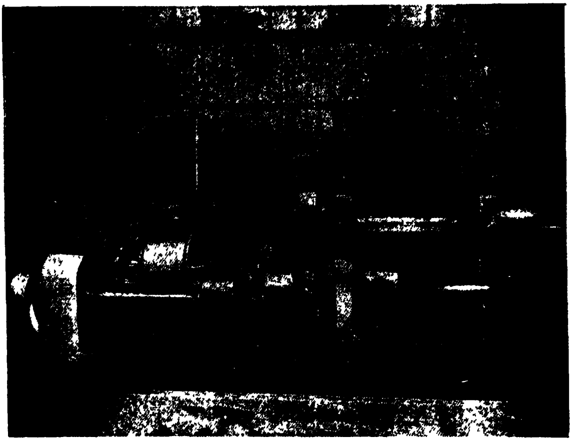


Fig. III. Illustration No. 1.

more efficient ones, and newer compounding ingredients replace the old. Accelerators, Anti-Oxidants and other added materials as fillers now give to rubber properties unattainable even a few years ago. That is the reason why Monsanto decided on the installation of their laboratory.

Such a laboratory, completely equipped, is not a small affair, and it is not easy to operate one efficiently. It serves in reality three distinct purposes: First of all, it is used to control the quality and uniformity of products being manufactured at the Chemical Works. It is secondly used to develop new products, and thirdly, it is used in a study of the adoption of these materials to meet the rubber manufacturer's specific needs.

As for the photographs so generously sent by the Monsanto Chemical Works, it will be observed even by a casual glance that very little, if anything, has been left to chance or rule—of—thumb in their installation. Complete recording instruments tell the story of what is happening at all times. Indicating dials, gauges and thermometers are used in profusion, and complete knowledge is obtained of everything that takes place. Only by such methods may one be assured of the uniformity of procedure or products. All the units of their manufacturing plant in their laboratory are thoroughly equipped for control of the various conditions such as temperature, time and pressure.

Illustration No. 1 shows the experimental Mixing Mill. It is in every respect a small size duplicate of an ordinary factory's mill, and every operation necessary in the factory can be carried out on this miniature mill. It is equipped with a safety brake operated by the rod overhead, which will stop the mill almost instantly. The rolls are provided with steam or cold water as conditions warrant. The equipment has an individual electric drive with an automatic overload controller motor, which permits of a heavy overload for a short period, or a light overload for a longer period without breaking the circuit.

Illustration No. 2 shows the hydraulic press equipment used for ordinary vulcanisation work. There are several features about this installation that are noteworthy. Each platen of each press has its own direct steam supply and condensation outlet, and in contrast to some installations, it is not necessary for the steam to pass through the two uppermost platens in order to reach the lowest one.

The moulds in use are of such size that they do not come nearer than four inches to the outer edge of the platens. The hydraulic equipment is designed for working pressures up to 3000 lbs. per square inch, though ordinarily from 500 to 1500 is used, depending upon the area of mould carried between the platens. Low pressure water supply of about 65 lbs. from the ordinary mains is used to operate the presses up the clossing point, and the high pressure is obtained by using the hand pump shown. This pressure is easily maintained over a cure of from 6 to 8 hours without touching the equipment.

The temperature control is of course automatic, and recording thermometers give written record of the temperatures at all times.

Illustration No. 3 shows an open steam vulcaniser. The piping only was not complete at the time the photograph was taken. The vulcaniser is provided with a quick-acting door of what appears to be an ordinary open steam apparatus. The vulcaniser is jacketed so that steam may be carried either in the jacket or in the inner chamber, thus permitting an open steam cure, or pan cure, if steam is in the inner

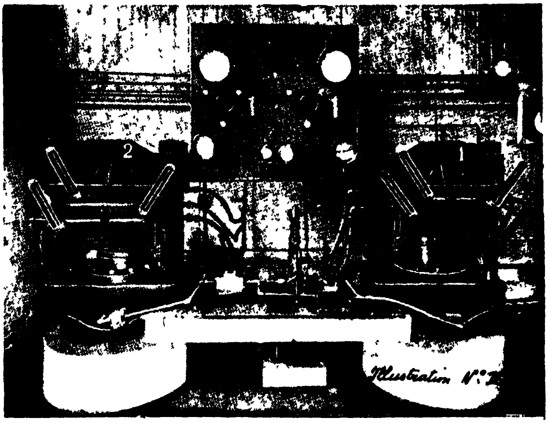


Fig. IV. Illustration No. 2.

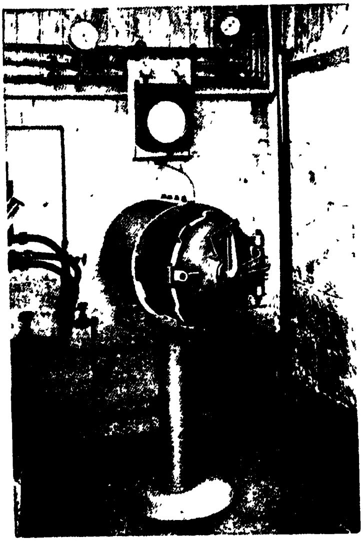


Fig. V. Illustration No. 3.

Fig. VI.   Illustration No. 4.

chamber, and also permitting of a hot air cure, if steam is admitted only to the jacket. A circulating fan is mounted on the rear of the vulcaniser to maintain circulation of the air inside of the heater. This air may be maintained under pressure so as to duplicate the factory condition utilised when vulcanising foot-wear under the usual air pressure of from 20 to 35 lbs. per sq. inch. The temperature control is automatic and a recording thermometer registers the details of temperature. There is a dual instrument which is shown directly over the vulcaniser.

Illustration No. 4 shows the Tensile Strength Machine and auxiliary equipment used to determine the tensile strengths and stress strain curves of vulcanised samples. On the machine one man is able to obtain data for stress strain curves. He holds in one hand the ruler to measure the elongation of the sample and at each 100 per cent elongation, presses a small electric button, which by means of a jump spark arrangement burns a small hole in the paper diagram shown on the top of the machine. After the test piece is broken, a record is copied of the actual pounds pull for each one of the burned spots in the paper chart. By shortening the radius of the sparking arm, a large number of test pieces may be run using the same chart.

The die and mallet used for stamping out the test specimens are shown at the left. The die is always kept wet with water and two or more layers of cardboard are held under the rubber sheet.

Illustration No. 5 shows one of the electrical ovens as well as the Williams type Abrasion Machine The automatically controlled electric oven shown, is used for the ageing of rubber samples according to the Geer Oven Test (Geer Oven Ageing Test, Rubber Age, New York 11,345 (1922)). The samples are suspended from the rotating shelf while the temperature of the oven is maintained at 70° C. plus or minus ½ degree. The shelf rotates about 30 times per minute, but this may be regulated to suit the conditions required. This rotation ensures a uniform temperature for all samples as well as agitating the air within the oven.

The Abrasion Testing Machine shown is described in the publication by Williams (Industrial and Engineering Chemistry 19,674 (1927)). This equipment is as originaly designed by Williams with the exception that the Prony-brake arm has been counterbalanced and thus eliminates the correction necessary for the weight of the arm. A continuous current of air at 30 lbs. pressure blows on the sandpaper disc to keep it clean and free from all rubber dust. Othewise, the machine is operated as originally described.

Illustration No. 6 shows one of the Flexing Machines used to determine the flexing properties of rubber. This is a comparative test machine, and absolute values are not relied upon. Each of the four wheels shown has slots for 12 samples, and these may contain from three to six pieces of the compound to be investigated and compared directly to the same number of pieces of a standard or known compound, which is mixed, vulcanised etc., under indentical conditions with the compound under investigation. This machine operates at about 600 R. P. M. giving some 1200 flexes to the samples per minute. The small rubber pieces extending from the steel discs have small grooves moulded in them, so that flexing always takes place at exactly the same position. Observations are made at regular periods and records are obtained showing when slight surface checking begins and when these small checks gradually grow into deeper cracks and when these deeper cracks extend through the rubber. Normally, the rubber compounds will stand from two to

Fig. VII. Illustration No. 5.

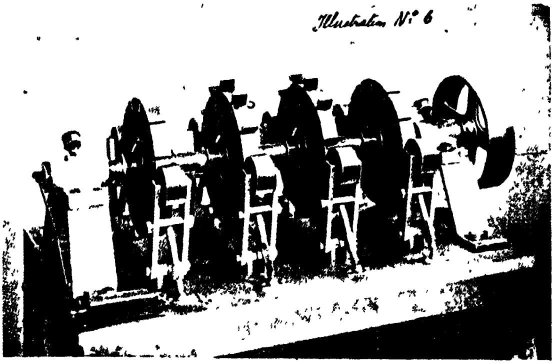


Fig. VIII. Illustration No. 6.

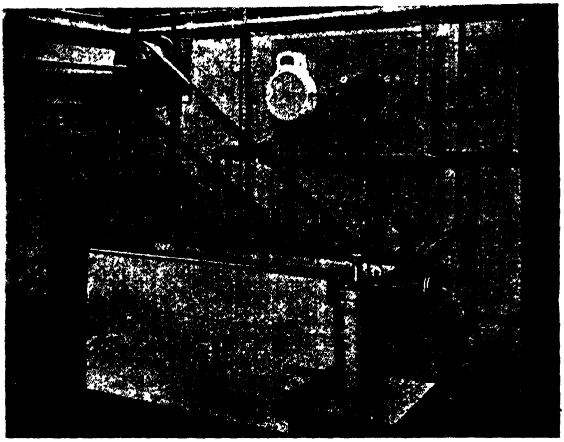


Fig. IX. Illustration No. 7.

ten million flexes in a machine of this type, this test occupying roughly from one day to a week. A revolution counter showing the number of flexes is shown at the left hand side of the machine. This machine has been conceived by the Monsanto Laboratories, the basic idea being derived from a machine of a somewhat similar type made by the India Tyre & Rubber Co., described in the *India Rubber World* in the July 1929 issue, page 62.

Illustration No. 7. shows the Oxygen Bomb testing equipment. The Oxygen Bomb Ageing Test was proposed by Bierer & Davis (Industrial Engineering Chemistry 16,711 (1928)). This equipment is operated normally at 70° C. and 300 lbs. oxygen pressure, which is a slight variation from the original specifications, but which is now standard for a large number of laboratories. In the equipment shown, there are five of the bombs, one being outside in a position to be unbolted. Each is supplied with oxygen under the proper pressure by the manifold lines shown in the photograph. The bombs are carried under water, the temperature of which is controlled automatically and is steam heated and circulated by a centrifugal pump shown at the right. The water is in mild agitation by the pumping action, and the temperature variation is less than one-tenth of 1° C. Oxygen is supplied from an ordinary commercial cylinder, one of which is shown on the left in the photograph.

Now that we have described the equipment of the Monsanto Laboratories, we might as well give the technical meaning of the expressions so often used when rubber manufactured goods have to be tested.

Tensile Strength K/cm² is the force required to break a strip of rubber, and denotes the strength of a rubber compound. Tensile strength provides also a means for determining the curing properties of the various parts in a given rubber compound.

Modulus is the term applied to the ratio existing between the deformation of vulcanised rubber and the load required to produce the same. It is reckoned in pounds per square inch at any elongation, or elongation at any given load. In tyre manufacture this is particularly important, as it is the measure for resilience.

Modulus is also synonymous with resistance to tear.

Hardness. The test of this property shows the rubber manufacturer the *tightness* of the vulcanisation, and is used mostly to detect either over or under cured conditions in various parts of the manufactured rubber article, due primarily to uneven heat distribution. These tests are made with the *Tinius Olsen Penetrometer*, an instrument which records the depth of penetration of a dull point under a given load into the surface of the cured stock.

The degree of *Plasticity* shows itself in unvulcanised rubber compounds, and serves to determine how they will process on the calender and the forcing machines.

The *Dispersion* of a given chemical in a rubber compound is of great importance to the rubber manufacturer, as the latter is particularly interested in the ease with which some fillers combine themselves with the raw rubber, so as to obtain uniformity in the rubber mixes. Unfortunately, there is no chemical, nor any physical test, which will give any data on this characteristic, and observation with the microscope is the only means available for determining this property.

With regard to other commonly used terms in the Rubber Industry, such as

Elongation %, or
Load at 700% elongation, or
Resistance to Abrasion, or
Ageing Properties,

these are too well-known to the Rubber Manufacturers to make any explanation desirable.

Other machines have also been invented for carrying out the above mentioned tests in the rubber laboratories. They are:

The Scott Model L. P., which is a Tensile Strength Testing Machine,
The Scopper Rapid Hardness Tester,
The Scopper Elasticity Tester,
etc. etc.

Specific Gravity. Before concluding this chapter, and with it the first part of this book, it is desirable that we should say a few words about specific gravity, as it plays an important part in the rubber trade, not so much in estimating the quality of a certain article, but in ascertaining whether two samples coming from different manufacturers will yield the same output, say the same length in the case of gas tubings and similar articles, or in the case of such goods as are bought by weight and sold by size or by piece.

Every day the rubber manufacturer is likely to receive enquiries for the supply of some kind of rubber goods, and it is only by knowing the specific gravity of the goods that he can fix a definite price for the article.

As an example, let us consider the case where a textile firm wants to know the price for re-covering one of their machine rollers, the dimensions of which are as follows:—length of the face 1 m. 800, diameter uncovered 300 mm., diameter re-covered with rubber 340 mm.

The following formula will give the weight of the used rubber:

$\frac{\pi H}{4}(D^2 - d^2)$ specific gravity = weight of the rubber. Applying this formula to the figures given by the textile firm, we get the following equation, it being understood, however, that to obtain weights in kilos, we have to convert the figures into decimeters, as a decimeter cube of water, which is the equivalent of a litre, weighs one kilogram.

$\frac{3.14 \times 18}{4}(3.4^2 - 3^2)$ specific gravity = weight. How to find the specific gravity of any rubber compound? The Nicholson Hydrometer (see fig. X) will help us in this direction.

The Nicholson Hydrometer is a hollow copper cylinder (C) with each end terminating in a cone (D) and (E). Cone E is connected to a disc (P) by means of a thin rod, whereas Cone D is attached to a conic container (K) filled with lead. The rod connecting P and E has a mark A, which corresponds to the point of the pin attached to disc P. When the apparatus is put in distilled water, it floats vertically, and will remain so in a state of permanent equilibrium on account of the container K being loaded with lead.

Now, we put weights on disc P, so that the apparatus gradually descends into the water until the mark A on the rod, which is the same as the point of the pin on disc P, reaches the level of the water. Let us call the total weight so obtained (M1). Removing then the weights from disc P and placing upon it a *dry* sample of rubber (M), the specific gravity of which we want to know, we shall have to add another batch of weights (M2) to attain mark A for the second time. It is clear then that the weight of the rubber sample M will be M1—M2.

Now, keeping the weights M on the disc P and removing the rubber sample from it, we place the latter

THE NICHOLSON HYDROMETER.

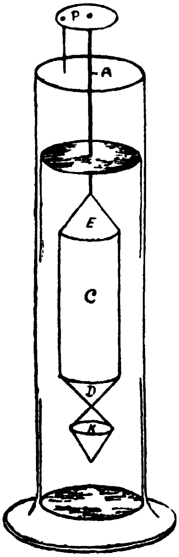


Fig. X.

in the water on the conic container K. The result will be that the apparatus will emerge from the water, and for the third time the mark A will be attained by placing additional weights on disc P, the batch of weights placed on the disc this time being M3, which represents the volume of the displaced water which is the same as the mass of the rubber sample, and we have the following equation:

$$\text{Specific Gravity} = \frac{M}{M3} = \frac{M1-M2}{M3}$$

An example will show more clearly the application of this equation:

Suppose we have to place 40 grams on the disc P for attaining mark A, 24 grams when the sample, of which we want to know the specific gravity, is on the disc, and 32 grams when the sample is in the water on conic container K. The mass of the sample will be 40 – 24 = 16 grams. When placing the sample in the water on container K, we have to add to the disc P 32 – 24 = 8 grams. Dividing 16 by 8, we get 2, which is the specific gravity of the rubber sample.

In conclusion and as per definition, the specific gravity is a relative value; it indicates by how much a given article is heavier or lighter than the volume of water at a temperature of 4° C., which it displaces. Strictly speaking, the article should be weighed at a temperature of 15° C. and the result calculated by the aid of factors, with water at 4° C. So accurate a method for ascertaining the specific gravity however, is not generally employed in the rubber industry. The article in question is simply weighed in distilled water at 15° C., and as already explained, the value found is subtracted from the weight of the article in air, the latter value being divided by the difference between the weights in water and in air.

Part II

CHAPTER I.

The Rubber Factory.

WHAT is needed for the efficient working of a rubber manufacturing concern:—

First, a well equipped factory with up-to-date machinery and accessories, and

secondly, a skilled technical staff for producing rubber goods.

A well equipped factory does not mean a factory with a lot of machines of different kinds, but one with adequate number of up-to-date machines provided with all the necessary adjustments to prevent accidents, as described in Chapter IX in connection with the miniature installation of the Monsanto Laboratories.

Mixing Rollers must be provided with a *Safety Brake* operated by a rod overhead, which will stop the mill almost instantly (see fig XI).

The Calender must have a safety brake operated by an electrical button, a simple push on which will stop the machine suddenly.

To check the temperature of the rolls of the Mixing Machines and the Calenders, thermometers specially designed for this purpose should be provided for the guidance of the workmen in charge of these machines.

Tubing Machines also should be provided with thermometers at the places reserved for them in the head of the machine as well as in the main body.

Vulcanisers and Vulcanising Presses should be equipped with manometers, with safety valves to regulate pressure, and also with condensing vessels allowing the condensed water to escape out of the vulcanising pans. A tap in the lid of the vulcaniser will permit the escape of air when the vulcaniser is filled with steam. A number of thermometers is necessary to complete the equipment, one of them being a recording apparatus registering the details of temperature and giving a graphic description of the way in which vulcanisation is taking place. Steam pipes should also be provided, where necessary, with manometers.

With regard to the Boiler in use in the Rubber Factory, it must have a superheater to secure as much dry steam as possible for vulcanisation purposes.

The factory building should be such that there is ample space between the machines, allowing workmen to move about freely.

The machinery in the factory should be installed methodically, so that the raw materials, delivered from the laboratory, enter the Works on one side, and, after passing through the various stages of fabrication, reach the other end of the factory in the form of finished goods, tested and ready for despatch.

In the laboratory, the chemist weighs the ingredients for the mixes following the adopted formulas, and they are brought into the Mixing Room, where they are mixed on heavy duty Mixing Rollers.

Mixing Rollers for making black mixes are generally installed in a separate room, thus preventing the interior of the whole factory from being covered with carbon black dust. There must be a tank with cold water next to each mixing roller, so that the ready mixes can be immersed in it for cooling.

A Warming Mill is situated near the calender. The mixes are warmed up on that mill for their calendering. The calender (see fig. XII) is a heavy duty machine with from 2 to 4 bowls, between which the rubber mixes pass to be reduced to sheets.

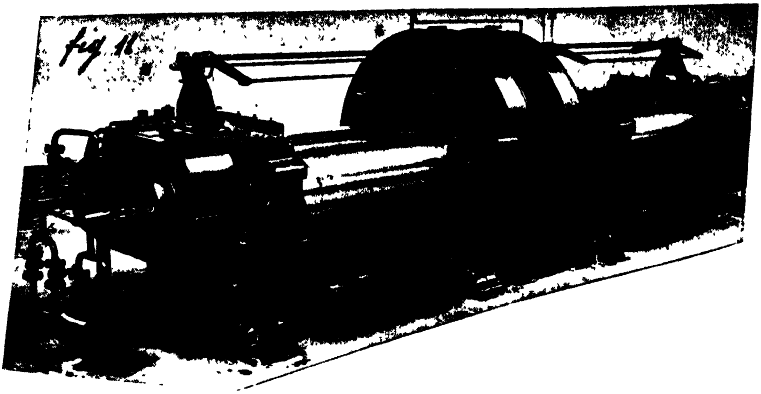


Fig. XI.

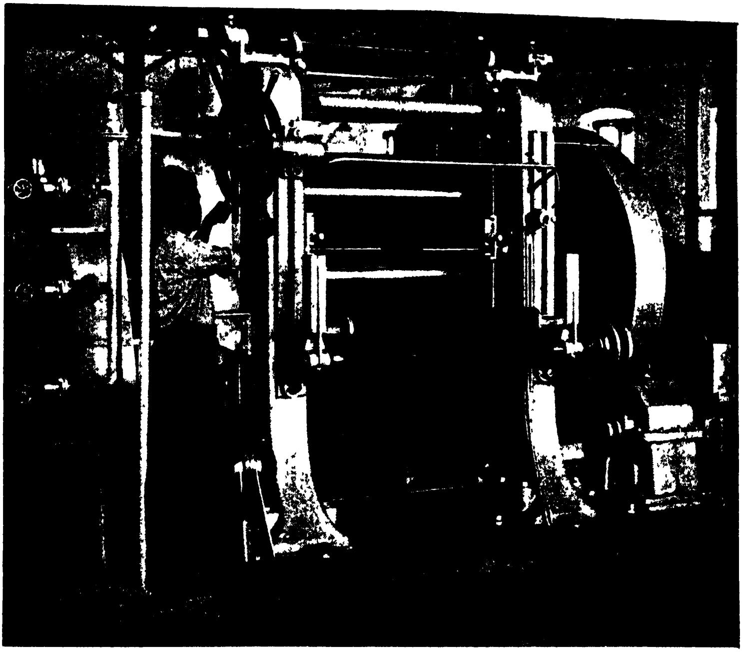


Fig XII.

Fig. XIII.

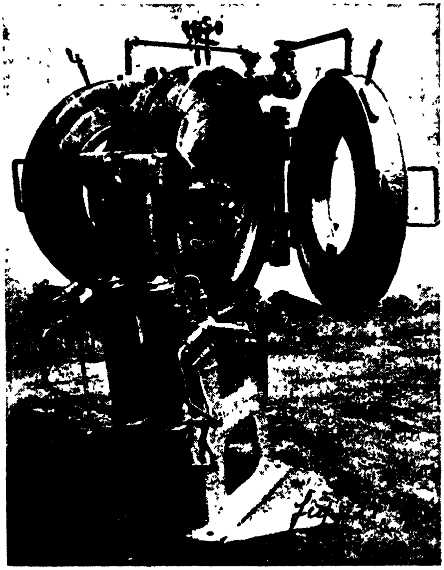


Fig XIV.

A small calender, also with four bowls, is installed in the vicinity for calendering thin sheets and principally the tyre treads. In front of the small calender is placed a longitudinal tank filled with water, so that tyre treads coming out of the calender may pass through it to be cooled and thereby prevent prevulcanisation.

The calender delivers sheets to the Sheet Making, the Moulding, and Hose Making Sections, whereas mixes coming directly from the Mixing Rollers are supplied to the Tubing Machine Section. These machines — also called Forcing Machines, and Extruding Machines (see fig. XIII) — are installed for producing rubber goods of various kinds. It is the size of the worm of these machines which determines the kind of goods they can produce.

A Tubing Machine of 30 mm. worm can produce mainly Valve Tubings.

A Tubing Machine of 60 mm. worm can produce surgical and gas tubings.

Both these machines have in front of them a turntable for receiving the extruded tubings.

Tubing Machines of 80 mm. are specially built for producing cycle tubes, etc.

The Tubing Machine of 150 mm. worm produces garry tyres, and motor car tubes.

Still bigger Tubing Machines of 250 to 350 mm. worm are used generally for straining reclaim rubber and certain special rubber compounds.

Conveying tables are placed in front of the Tubing Machines of 80 mm. to 350 mm. worm, and all these machines are provided with talcum devices.

The tyre building section houses the Watch Cases (see fig. XIV) built for the vulcanisation of tyres.

In the sheet making section, the sheets with their insertion of cotton, asbestos or metal are rolled on drums and wrapped with fabric for their vulcanisation.

The vulcanisers are of various sizes and dimensions. For vulcanising sheets and bicycle tubes (see fig. XVI) they are not less than 5 ft. in diameter and 10 ft. in length. Rubber hoses are cured in vulcanisers, sometimes 100 ft. or more in length. These vulcanisers are fitted with inside rails connecting railways placed on the floor of the factory. The lids of vulcanisers are now-a-days boltless, and close by a patented *bayonet system* (see fig. XVII).

The vulcanising section is also provided with Hydraulic Vulcanising Presses (see fig. XV) having from 1 to 10 daylights. Moulded goods are vulcanised in such presses. Those for vulcanising garry tyres have a total length of about 23 ft., whilst others are 5 ft , in width with a total length of about 33 ft., and these special presses with their stretching devices are intended for vulcanising belts of various sizes. (see fig. XVIII).

In the Rubber Hose Section, there is a machine for making hoses with insertion, or with spirals, and for wrapping the ready made hoses for vulcanisation.

Braiding Machines are a part of the equipment of that section, for braiding special rubber hoses. (see fig. XIX.)

The Rubberising Machines and the Solution Mills are housed in special rooms.

Tables are placed in the various sections for working purposes. In the sheet making section, these tables are 5 ft. wide and up to 50 ft. long, whereas in the Rubber Hose section the tables are generally 3 ft. x 100 ft.

Machines for cutting washers, rings, and erasers, grinding stones and lathes are the necessary complement of a rubber factory.

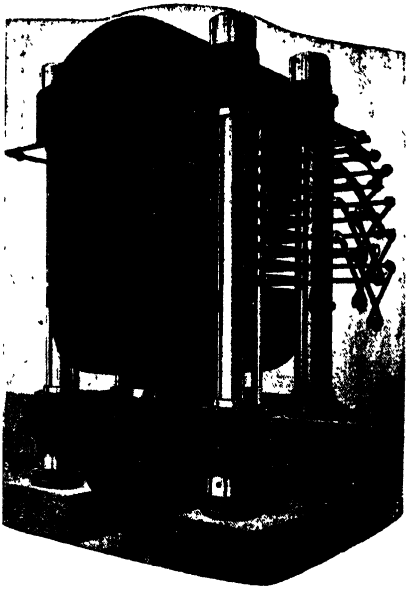


Fig XV.

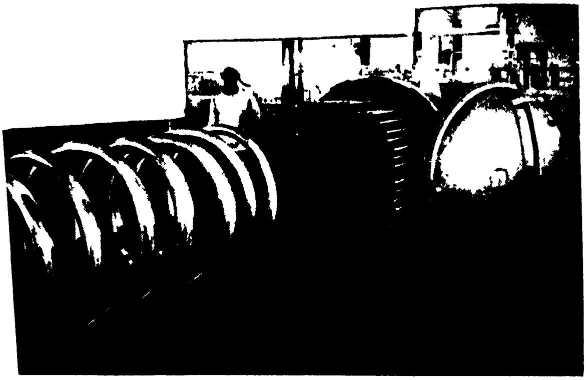


Fig. XVI.

Fig. XVII.

Fig. XVIII.

Fig. XIX.

In a special section, where the latex is worked, there should be Ball Mills, Mixing Apparatus and machines for producing all seamless articles such as balloons, teats, gloves and the like.

The last section should be the place where the finished goods are tested, checked and packed for delivery.

The boiler and boiler house must be outside the factory.

The question now arises as to the best motive power to be used for running a Rubber Factory. Many will suggest oil engines, whilst others will think of electrical motion, and a few will prefer the steam engine. Let us consider these three motive powers.

Why the oil engines? For the reason that they run easily without much supervision, and the necessary fuel can be had at a reasonable price.

Why then the electrical motors? Nothing is as simple as running an electrical motor. All that is required is just a push on a button, and you consume only the power you really need, and not the full power for which the motor has been built.

What about the steam engine? For running it, one needs a boiler, and it so happens that a boiler is a vital part of any Rubber Factory. Without a boiler, no vulcanisation of rubber is possible. Then why not have a boiler of sufficient capacity, to supply steam not only to the various vulcanising apparatus, but also to a steam engine? The maintenance of a boiler is a necessity in every rubber factory, and a fireman is needed for working it, whether it is capable of producing 100 lbs. or only 20 lbs. of steam pressure. The cost consumption of a slightly larger quantity of fuel is the only additional expense in running a steam engine.

In conclusion electrical motors are only preferable to steam engines in cases where electrical power is available at very low rate.

CHAPTER II.

Manufacture of Dipped Goods from Rubber dissolved in Solvents.

IN studying the manufacture of dipped goods, let us consider the fabrication of an item which at first looks very easy to produce. For, there seems to be no difficulty either in masticating raw rubber on the Mixing Rollers, or in dissolving it in the solvent. Nor is there any apparent difficulty in making balloons, teats, gloves and other seamless articles, if one has the required procelain moulds. No difficulty! At least so thinks the layman, and many others who call themselves *Rubber Technologists*, but have no thorough knowledge of the rubber making process.

No difficulty!

Unfortunately, as soon as the *amateur fabricant* starts his dipped goods business, he encounters a lot of difficulties. The dipped goods, when emerging from their bath, are full of bubbles, and the moulds do not break away.

What is the reason for this trouble? The amateur rubber manufacturer, of whom we spoke, might explain that he has twice masticated the raw rubber, but for how long he did masticate the rubber, he could not say. All he knows is that as the masticating work proceeded, the rollers of the Mixing Machine became increasingly hot, which was regarded by him as fortunate, in that the time required for masticating the rubber was thereby considerably reduced, and he thought he could finish the job in say 20 to 25 minutes. When the rubber was thus being masticated, it was dissolved in petrol—the ordinary motor car petrol!

Whether this petrol was suitable for this particular purpose, and what its boiling point was, the so called rubber technologist once again cannot say. He just simply wonders why he is experiencing so many difficulties.

Let us consider these difficulties and try to find a remedy for them.

It is a fact that the occurrence of air bubbles in dipped goods is frequently due to various causes, and it is important that every stage of the fabrication should be carefully checked.

The process of masticating the rubber should be thoroughly understood. The work must be accomplished on rollers, the temperature of which should not exceed 60° C., so that the rubber may not be viscous owing to the excess heat of the rollers. The time for masticating should not exceed 40 to 45 minutes, and the rubber, to be dissolved, should not be tough. In order to reduce the toughness of the rubber, a *softener* (vaseline oil, paraffin oil, or *Palatanol*), say 2% of the weight of the rubber, should be added to the mix. When the rubber is well masticated on rather cool rollers, it should be dissolved immediately in the solvent. In what kind of solvent? *Tetrachloride of carbon* is the best for this purpose. Besides it is *non-inflamable.* A good solvent for dissolving the rubber should have a boiling range of between 194° and 266° F. Components with a lower boiling temperature than 194° F. may easily cause blisters during the drying of dipped goods. Also there should not be any substances in the solvent boiling only at over 266° F., as they evaporate too slowly. It has been found by experience that a solvent with a high boiling point creates air bubbles inside the manufactured product, whilst a too light solvent creates air bubbles on the top of the mould, called the *breaking-off point.* This is due to the quick evaporation of the solvent during the dropping off of the solution.

For ascertaining whether the solvent to be used agrees with the limitations imposed, it should be checked according to the *Engler-Ubbelohde* method with the boiling apparatus in use for Customs purposes, and sometimes one finds surprising deviations.

Solutions for dipped goods, which are too viscous, or do already contain air bubbles as a result of the stirring process on the *Stirring Mill* should be perfected by being poured into the dipping tank and being allowed to remain there for at least 24 hours before starting with the dipping of the moulds, so that the air in the solution may reach the surface and escape.

It must also be borne in mind that mixtures of varying degrees of mastication result in solutions of different mobility, the more processed mixes resulting in móre liquid solutions. The rubber and solvent should be taken in the proportion of 1 part of rubber to 7 parts of solvent, and in order to obtain uniform qualities, working conditions in the factory and the concentration of the compound, once found suitable, should be strictly adhered to.

A good solution must never be too thick and must run well. The moulds should be lifted out of the dip-solution *as slowly as possible*, so that the latter runs off, as the level of the solution recedes to avoid dripping, which would cause air bubbles in the solution in the tank. At the most one drop of solution may remain on the top of the mould. A good precaution to prevent the effects of dripping is to keep a galvanised sheet under the mould so that if by chance the solution drips off, the drops may fall on the sheet, and not in the tank.

In the case of goods requiring more than one dipping, the first dip must be thoroughly dried before dipping is continued, as the solvent, if only partially evaporated, will produce air bubbles between the different layers of solution.

When dipped goods are produced by means of a *Dipping Machine*, care should be taken that the temperature of the machine varies between 25 and 30° C. only.

The following is a loaded mix for ordinary gloves and teats:

Pale crepe twice masticated	10^{k} 000
Zinc Oxide active	0^{k} 100
Sulphur	0^{k} 220
Whiting from	15^{k} to 30^{k} 000
Vulkazit P extra N	0^{k} 100
Cadmium Red	0^{k} 180
Vaseline Oil	0^{k} 200

Cure in hot air: 45 to 50 minutes at 110° C. (230° F.)

Another mix recommended for teats:

Crepe twice masticated	10^{k} 000
Colloid Zinc Oxide	0^{k} 200
Stearic Acid	0^{k} 100
Vaseline Oil	0^{k} 200
Sulphur	0^{k} 275
Monsanto Accelerator A32	0^{k} 025

Vulcanisation: 30 to 45 minutes at 286° F. (141° C.)

Teats and other seamless goods can also be made from solutions without accelerators. Goods made from such solutions are immersed for 4 to 6 seconds in a solution of accelerators of 10 grams Vulkazit P plus 10 grams Vulkazit 774 dissolved in a litre of benzine. When the solvent has completely evaporated, the goods are vulcanised in hot air for 40 minutes at 110° C. or 230° F.

To obtain the rather thick walls required in the case of teats, 6 to 8 dippings are necessary. After the moulds have been dipped three times, and the solvent has completely evaporated they are dipped in the accelerator solution for a few seconds, after which they are again dipped in the rubber solution until the desired thickness has been obtained. After the final dipping, and when the solvent has entirely evaporated, the goods are once again dipped in the accelerator solution and then vulcanised in hot air for 40 minutes at 110° C. or 230° F.

Dipped goods made from solution without accelerators can be vulcanised also in a saline solution of 10% NaCL, which is cheaper than the accelerator solution. The goods are immersed for 30 minutes in the saline solution heated at 95° C. The dipped goods, after immersion in the solution of accelerators, can also be vulcanised in open steam. But, to avoid the condensation of steam on the manufactured goods, which may cause spots, the vulcaniser should be heated before the dipped goods are introduced into it. For this purpose, steam is let into the vulcaniser for 5 minutes at 110° C. or ½ atm. and is kept there for another five minutes, after which it is allowed to escape, the vulcaniser remaining closed for another 5 to 10 minutes, after which the goods are introduced into it, where they are cured at 286° F. for 30 minutes.

Dipped goods, when vulcanised, are removed from their moulds by dipping them in a solution of benzine with talc or starch.

The following is a mix for *Surgical Gloves.*

Pale crepe twice masticated	10^{k} 000
Zinc Oxide active	0^{k} 060
Sulphur	0^{k} 180
Vulkazit P extra N	0^{k} 080
Vaseline Oil	0^{k} 200

Cure in water: about 30 minutes at 95° C.
Cure in steam: about 25 minutes at 110° C. (230° F.)

Such gloves can stand more than 100 sterilisation under normal conditions, namely 20 minutes at 120° C.

Mixes for *Electrical Gloves.*

(1)	Crepe twice masticated	10^{k} 000
	Zinc Oxide	0^{k} 500
	Sulfate of Barium	2^{k} 800
	Paraffin Wax	0^{k} 075
	Sulphur	0^{k} 200
	Ureka	0^{k} 250
	Red Iron Oxide	0^{k} 500
	Vaseline Oil	0^{k} 200

Cure in water: 90 minutes at 100° C. (212° F.)

(2)	Crepe twice masticated	10^{k} 000
	Zinc Oxide	0^{k} 300
	Silicious Chalk	15^{k} 000
	Paraffin Wax	0^{k} 075
	Sulphur	0^{k} 200
	Ureka	0^{k} 200
	Red 3 E	0^{k} 150
	Vaseline Oil	0^{k} 200

Cure in hot air: 10 minutes at 200° F. plus
75 minutes at 250° F. (121° C.)

(3)	Crepe twice masticated	10^{k} 000
	Stearic Acid	0^{k} 100
	Soft mineral rubber	0^{k} 500
	Ozokerite	0^{k} 100
	Zinc Oxide	2^{k} 500
	Vulkazit DM or Rapid Accelerator 201	0^{k} 100
	Vulkazit Thiuram or Rapid Accelerator 501	0^{k} 300
	Anti-oxidant MB	0^{k} 050
	Vaseline Oil	0^{k} 200

Cure: 25 to 30 minutes at 2½ atm. or 138° C.

Electrical gloves should be completely free from blisters, holes or mechanical defects. Each dipping must be checked for this purpose and every single glove must be carefully tested before despatch.

The following is a transparent mix recommended for balloons and other seamless articles with very thin walls:

Crepe twice masticated	5^{k} 000
Zinc Oxide active	0^{k} 030
Sulphur	0^{k} 090
Vulkazit P extra N	0^{k} 040

Cure in water: 35 minutes at 98° C. (208° F.)
or in steam: 15 minutes at 281° F. (138° C.)

Generally, two dippings in this solution are required for producing resisting balloons.

Balloons of American origin have inside the mouth piece an *unvulcanised layer*, which makes it possible to close the baloon by pressing the mouth piece. In order to obtain such fabrication, a layer of rubber solution with neither accelerator nor sulphur should be applied inside the mouth piece after the balloons have been vulcanised.

Printing of Designs on balloons is done by using a rubber solution containing a fairly large quantity of pigment colour. For this process, the balloon should be slightly inflated, and the rubber solution must either be sprayed thinly with the help of stencils, or be printed from a stamping pad.

The following is a printing mix:

Pale Crepe twice masticated	100	parts.
Titandioxide (lithopone)	50	„
Vulcan colour powder	50 to 100	„
White Gloria Factice	100	„

The mixture must be swelled in white spirit and then diluted with white spirit, the quantity of spirit necessary being dependent on whether the printing is done by means of a stamping pad or by spraying.

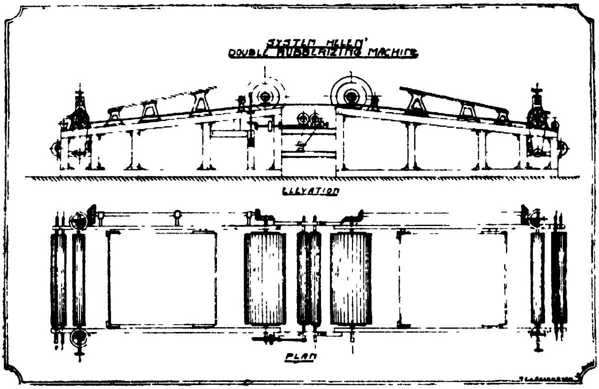
Balloons and other dipped goods can also be made from latex mixes. This will be discussed in Part III of this book.

CHAPTER III.

Proofed Fabrics.

PROOFED Fabrics for raincoats, hospital sheetings, paulins, groundsheets etc. are made by applying the solution to the fabric on the Spreading Machine. In the case of doubled fabrics, when sufficiently coated, they are assembled on the Doubling Device and finally vulcanised. The vulcanisation can be done either by steam or in hot air, by cold process, or with the combination of an ultra-accelerator. In the latter case, vulcanisation is done at room temperature in 7 to 14 days.

It may be pointed out here that when in the course of these pages *cure in hot air* or *cure in steam* are mentioned, *cure in hot air* is applied to such articles as cannot stand the direct contact with steam. As has already been stated, rubberised fabrics can be cured in steam, wrapped up in waterproof covering, which will protect them from the effects of steam. They can also be vulcanised in the hot air of a double jacketted vulcanising pan or, better still, in an electrically heated room. Such a room, or the *Electric Vulcanising Apparatus* as it can be called is made of strong wooden walls with the inside covered with two layers, the first of asbestos and the second of copper sheets. The apparatus should be large enough to contain a drum on which the rubberised fabric to be vulcanised is wrapped. The temperature of the room should be maintained at 150° C. either by electric heating units or by carbon filament lamps of 32, 16 and 8 candle power. The carbon filament lamps are preferable to electric heating units, because the temperature can be modified by the addition or removal of one of the filaments either of 32, 16 or 8 candle power as the case may be.



Double Rubberizing Machine. (System Helen) Fig. XX.

The author has designed a Double Rubberising Machine with Doubling Device (see fig. xx). This machine works as stated below.

Whilst the muslin is rubberised on one part of the machine, the sheeting is rubberised on the other. When the fabrics have been sufficiently coated, and well dried by passing over heated chests and rotating drums, they are doubled by passing them between the heated rollers of the Doubling Device, after which, in case they have been coated with an ultra-accelerator solution, they are allowed to continue their vulcanisation in room temperature, which takes a few days. They can also be vulcanised either in hot air or open steam, these two processes of vulcanisation taking only a few minutes. For steam vulcanisation the rubberised fabrics are well wrapped in a protective envelope, also called *Liner*, so that the steam may not attack the rubberised fabrics.

As an ultra-accelerator, the *Monsanto RN 2* can be recommended for solution dissolved in a solvent, and for latex mixes as well. In part III, we shall have some more theoretical details about accelerators used in latex. In this chapter, let us just say that RN 2 is a rubber soluble liquid accelerator capable of giving exceptionally fast cures at low temperatures. This accelerator finds its application in self-curing rubber cements.

RN 2 is too active an accelerator for milling on ordinary mixing rollers, and cannot be processed without scorching. Two solutions must therefore be compounded as follows:—

A.	Rubber	100	parts
	Sulphur	6	,,
	Stearic Acid	1	,,
B.	Rubber	100	,,
	Zinc Oxide	10	,,
	RN 2	1.5	,,

Other additions may be made to each stock, but the above represent the basic formulas to be used in making quick-curing or so called *self-vulcanising cements.*

Self-vulcanising Cement is an expression which is now very commonly used, but it must be realised, however, that in practice no such cement, which is capable of self-vulcanisation, does really exist. For, if a single cement is to have the power of self-vulcanisation, its cure should start from the very moment of its fabrication and complete cure will have taken place after a few days in room temperature, with the result that such a cement will be quite useless from the time it is out of the factory! As has been stated, two cements, one containing sulphur and the other containing ultra-accelerator, should be combined together, and by their combination they will have a vulcanising power. These two cements should, however, be kept separate and be mixed together only for immediate use. It would still be better not to mix them at all, but to apply them separately. The composition of cements which may self-vulcanise in a given time is a very difficult affair, as it depends on the correct proportion of the vulcanising ingredients which will have to be incorporated in it. For instance, such cements may vulcanise correctly in 24 hours and will still continue to vulcanise if there is an excess quantity of sulphur present. The result will be that the cement will get overcured in another period of say 24 hours and may still continue to vulcanise until all the free sulphur and the accelerator combines with the rubber solution, producing finally a self-vulcanising cement so overcured that it would look like a sort of *ebonite.* If on the contrary, the sulphur content is very much reduced so as to prevent an overcure of the cement, self-vulcanisation can be effected only very slowly, requiring rather a long period of time. For producing a satisfactory self-vulcanising cement therefore the chemist should work up a formula which is midway between these two extremes. The chemist will still have other difficulties besides the above, in compounding such a self-vulcanising cement. The choice of a suitable accelerator is also highly important. If, for instance, one is using a rubber soluble accelerator, it will migrate into the rubber on which it is applied, and the accelerator will gradually free itself from the cement with the result that the latter will not self-vulcanise at all! The best thing to do in such cases, says Monsanto, is to use their *Ultra Zinc D. M. C.*, which is a non-migrating accelerator of the zinc salt group, and the two formulas suggested should be made up as follows:

A.	Rubber	100	parts
	Sulphur	6	„
	Stearic Acid	1	„
B.	Rubber	100	parts
	Ultra Zinc DMC	2	„
	Zinc Oxide	10	„

Fillers as may be required can be added to both the above formulas. The combined cement will vulcanise in room temperature in about 2 days; in hot air at 140° C. in 2 minutes; and at 115° C. in 4 minutes. It is possible also to obtain a fairly good cure in 2 hours at 80° C.

The Imperial Chemical Industries recommend their *Vulcafor Z D C* for the same purpose. It is said to be an ultra-accelerator of the zinc diethyldithiocarbamate group and is most active in general use, having a wider curing range than any other product available. It can be used for cures in the neighbourhood of ordinary room temperature and also for cures at 70 or 80 lbs. steam pressure. Naturally, in order to prevent scorching, an accelerator of this activity demands particular care in handling, but the I. C. I. write

> "that it is today being used without"
> "difficulty even in factories which have only a"
> "moderately efficient cooling system. For"
> "ordinary press curing purpose, it is usual to"
> "use from 0.25 to 0.375 parts of ZDC and"
> "about 2 parts of sulphur with each 100"
> "parts of rubber in the mix. With heavily"
> "loaded mix, it is usual to use slightly"
> "increased quantities, which is also the case"
> "with hot air curing work."

With *Vulcafor ZDC*, just like with *Ultra Zinc D. M. C.* and *RN 2*, two different mixtures should be made, the one containing the sulphur and the other one the ultra-accelerator, and as already said, as long as these two mixtures are kept separately, they may be stored indefinitely for any length of time without any change in their properties, vulcanisation starting only when they are mixed together.

The *Double Rubberising Machine System Helen* has been designed for the purpose of using the two aforesaid solutions A and B simultaneously.

The muslin is coated with solution A on one part of the machine, whilst the sheeting is coated with solution B on the other, and both the fabrics are doubled through the *Doubling Device*, which is a part of the Rubberising Machine. Now as solutions A and B join together, their vulcanisation starts by contact, at room temperature say in 7 to 14 days. If they are cured in steam, a few minutes at 50° C. will suffice. As already explained, to vulcanise the fabric, so rubberised, in open steam, the proofed goods should be wrapped in a waterproof fabric on a drum, so as to prevent the steam reaching the fabrics. A hood installed above the Double Rubberising Machine will collect the vapours produced by the heated solvent, and these vapours are condensed by passing through a serpentine in a cooling tank so as to recover most of the evaporated solvent.

Acid proof Hospital Sheetings are made on the same Rubberising Machine, employing the following formula:

Crepe twice masticated	10^{k} 000
Zinc Oxide	0^{k} 500
Lithopone	2^{k} 500
Sulfate of Barium	3^{k} 000
Silicious Chalk	7^{k} 500
Sulphur	0^{k} 225
Ureka White	0^{k} 160
Paraffin Wax	0^{k} 200

Cure in hot air: rising for 90 minutes and keeping further 50 minutes at 250° F. (121° C.)

There is another way of proofing fabrics without using a rubber solution, i.e. the *Friction Method.* This is done on the calender, and is rather a difficult process, requiring skilled and long experienced workmen for efficient execution. A very plastic rubber compound is required, when fabrics are frictioned on the calender. The raw rubber is masticated for half an hour on cold rollers slightly opened, the rollers being gradually tightened as work proceeds, so that when the first operation of mastication is over, the rollers are fully tight. Then the rubber is taken from the Roller and allowed to rest for 24 hours. Next day the rubber again undergoes the same process of mastication for half an hour, and is again taken from the roller and allowed to rest for another period of 24 hours. The raw rubber is now ready to be incorporated in the mix, which when terminated is also allowed to rest for a further period of 24 hours, and it is only then that the process of frictioning the fabric on the calender can be started. For this, the ready made mix is softened on the Warming Mill. A few drops of *Tetraline*, added to the compound, will facilitate the friction of the fabric. Tetraline, chemically Tetrahydro-Naphtalene, is a solvent, which explains its use for frictioned stocks. The mix so ready is then introduced into the calender, between the upper and the central cylinders, the three cylinders of the calender having been warmed up, the upper one at a temperature of 42° C., the second at 67° C., and the lower at 50° C.

The temperature of the central roller makes the mix to run round it. When the man in charge of the calender feels that the rubber has attained the desired degree of plasticity, the cloth is introduced between the central and the lower cylinders, the rollers so distanced as to prevent the fabric from being torn. Care has to be taken that the calender is continually supplied with more mix till the fabric is completely rubberised.

Gofferdam Plates are obtained from the following formula, dissolved in a solvent:

Crepe twice masticated	5^k 000
Smoked sheets twice masticated	5^k 000
Zinc Oxide Active	0^k 050
Vulkazit P Extra N	0^k 060
Mineral Oil	0^k 350
Stearic Acid	0^k 100
Sulphur	0^k 180

Cure: 30 minutes at ½ atm. or 110° C. (230° F.)

For the preparation of the above mix, it is suggested that the accelerator, together with stearic acid, is incorporated in the rubber at the beginning of the mixing process, zinc oxide, sulphur and mineral oil being added when the others have been well mixed in the rubber.

The oldest method of manufacturing Gofferdam Plates, and the one which is usually employed in factories where the manufacture of these goods is a speciality, is to spread the above mix on the Rubberising Machine. This process of manufacture has its undoubted advantages, but is considerably more expensive on account of the enormous quantities of solvent required and the greater amount of labour involed. The sheets are of a homogeneity and purity hardly attainable with any other method. With spreaded sheet, the Rubberising Machine takes the place of the calender. Four rubberising machines are considered to be necessary for a daily production of 120 kilos of sheets.

The process of manufacturing these sheets is as follows:—

Well masticated cleaned rubber is dissolved in solvent and then worked up in the solution mill until a clear solution, free from lumps, is obtained. The solution is further diluted with more solvent according to the thickness of the sheet to be produced.

The rubber for the sheet is spread on a specially prepared rubberised canvas. The closely-woven fabric used for this purpose is impregnated with solution, then vulcanised and afterwards covered with a thin layer of shellac.

The Gofferdam plate is then spread on the smooth layer of shellac. When the sheet is completed, it is stripped off, powdered with talc and vulcanised.

The shellac coated rubberised fabric, as soon as the surface is worn off, must be cleaned and freshly coated with a new layer of shellac. To vulcanise the Gofferdam Plates, they are wrapped in vulcanised twill proofed with a solution of pure rubber with accelerator and sulphur. This sort of twill can only be used twice or thrice for this purpose. Afterwards, it is sold as proofed cloth. The vulcanisation takes place in a water-bath at the indicated temperature, care being taken that an absolutely uniform temperature is maintained. After vulcanisation, the sheet is unwrapped and well washed in water with soap.

Observatory Balloons are often made from unvulcanised Gofferdam plates. Manufactured by hand, the edges well stuck together, they are cured in talc 30 to 40 minutes at 110° C. (230° F). The fabrication of Gofferdam Plates and the manufacture of Observatory Balloons from these plates is extremely difficult, necessitating the employment of experts and trained men. If they are not available in the factory, it would be better not to undertake any such fabrication.

Proofed Canvas, for insertion in rubber sheets for the fabrication of rubber hoses and for the manufacture of bicycle tyres and the like, is usually rubberised on the Rubberising Machine, but, when skilled labour is available, it is sometimes frictioned on the calender.

CHAPTER IV.

Manufacture of Rubber Hoses.

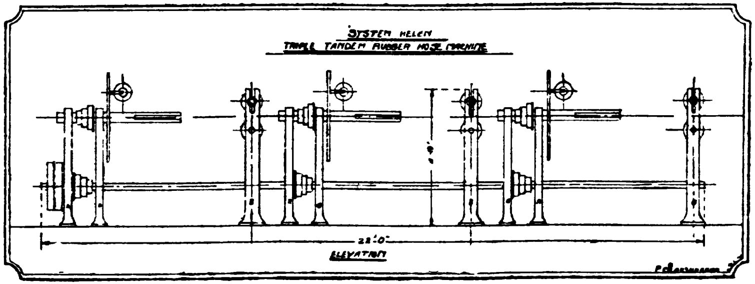
AMPLE space should be reserved in the factory for the Rubber Hose Section, where pillars or other obstacles should not stand in the way, in order that the mandrels, sometimes as long as 100 ft., on which the hoses are built, can be transported without hindrance from one place to another: to the Rubber Hose Machine and from it to the *chariot* for carrying the hoses in the vulcaniser.

As a rule, the inner rubber layer of the hose is extruded on the Forcing Machine, then mounted on the mandrel for further processing. This method is disadvantageous for the reason that by uneven mounting on the mandrel, some parts of the inner tube become thin, and this produces hoses of bad construction.

The best method, but for an unfortunate drawback, would be to have the rubber forced round the mandrel, which passes either through the perforated worm of the tubing machine or through the right angle head, specially constructed for that purpose. By this method, not only is labour reduced to a minimum, but even thickness of the inner tube is maintained throughout its length. The drawback is that it is quite impossible to introduce the talc between the rubber tube and the mandrel on which it is built, with the result that, after vulcanisation, it is rather difficult to remove the hose, combined with its insertion, from the mandrel. For this reason, the said method is not to be adopted. The one of early days apparently seems to be the best. In fact, it is still in use in many of the rubber factories we know. By this method, the rubber sheet is drawn on the calender, then cut to the required size, the inner side dusted with talc to prevent its sticking to the metal, and so the rubber layer, its edges well-cleaned with benzine, is placed round the mandrel, the overlapping part pressed with the fingers and then rolled with a special tool.

When this is done, the second stage of the fabrication commences, i. e. wrapping the inner tube with the required insertion. This can be done by hand. The rubberised fabric is cut diagonally at a given width according to the number of plies and the circumference of the hose to be manufactured. The cut pieces are joined end to end, well pressed together, and rolled on the inner tube with special care, so that no air remains between the rubber and the wrapped cotton or between the plies of the latter.

There is another system for placing the rubberised fabric on the inner tube, which is possible with the Triple Tandem Rubber Hose Machine designed by the author (see fig. XXI.) This machine has three discs, the first one rotating from right to left, the second one from left to right, and the third one again from right to left. The mandrel with the inner tube passes through the centre of the discs, and by a certain device is pulled forward at a given speed. On each disc is placed a roll of rubberised fabric, to which, by means of a brake, the required tension is given, so that the plies cover the rubber tube spirally, well tight. The rubber fabric is rolled longitudinally to this effect, the warp and the weft being of the same yarn and cut just like an insulating tape at a given width. The machine is then put in motion, the cotton tape from the first disc overlapping the tube from right to left, the second one from left to right, and again the third one from right to left, the rubber tube being thus crossed and overcrossed, giving an insertion of plies of an indisputable strength.



Triple Tandem Rubber Hose Machine. (System Helen) Fig XXI.

The third stage, placing the upper layer of rubber over the cotton fabric, can be done on the Forcing Machine, the hose passing through the right angle head or the perforated screw, as the case may be. Finally the hose is brought again to the Triple Tandem Rubber Hose Machine on which it is then bandaged with two to three plies of ordinary but fine unrubberised fabric at the required tension, so that after vulcanisation the hose has a fine round shape, uniform throughout with an impression of the fine cotton fabric visible on its surface.

Some rubber hoses have to resist steam, air or water pressures. In such cases the cotton plies are combined with braided cotton alternating with braided brass wire, well coated with solution. Such rubber hoses pass through a container filled with solution. Interchangeable nozzles can be fitted to the outlet, their sizes being dependent on the external diameter of the hose. In the interior of the nozzle is a soft rubber cork with a central opening capable of squeezing the hose which passes through it, so that no excess solution remains on it. By this process, the solution is well pressed into the meshes of the cotton yarn and copper wire, and an exceedingly close adhesion will exist between the various rubber coated braided plies of the hose. An upper layer of rubber completes the hose, which is then wrapped in ordinary fabric and vulcanised. Rubber hoses so manufactured are able to resist very high pressure, say up to 100 atm., provided they have the required number of braided plies, proportionate also to the internal diameter of the rubber hose. Different braiding machines are used for different sizes of rubber hoses, but the braiding should not be too loose or too close or too long, the best braiding being the one in which the yarns cross at right angles.

Spiral Hoses. In the manufacture of this kind of hoses, the position of the spiral depends on the purpose for which the hose is intended, whether for *suction* or for *delivery* or for both, and the spiral must be placed inside, outside, or in the middle to meet the particular requirements. For suction hose, the spiral, which is best made of moderately hard galvanised wire, is placed first on the mandrel, whereas for pressure hoses a sheet of rubber is placed first round the mandrel, over it the required number of canvas plies and finally the spiral. Formerly, when the wire was run on to the hose by hand, the rubber layer was often badly twisted or even torn in consequence of the running and subsequent re-extension of the wire, but now-a-days special machinery is used, by means of which the wire is given a suitable spiral form. It is then slipped either directly on the mandrel in the case of suction hoses, or on the plies in the case of pressure hoses. This is far safer and more rational than the old fashioned method. Both ends of the spiral are then tightened and kept in position by means of a strip of vulcanised rubberised canvas. Over the spirals is a layer of rubber, and upon this the rubberised canvas. For smooth surface spiral hose, the interspaces of the wire are filled with strips of rubber over which the canvas plies are placed, and finally a layer of rubber. Then, as previously mentioned, the hose is wrapped on the Triple Tandem Rubber Hose Machine. In the case of suction hose, where the outer appearance of the hose is intended to give an indication of the spiral inside, a cord of sufficient thickness is laid tightly by hand in the interspaces of the spiral. After this cording process, vulcanisation takes place in the heater in the same way as for other hoses. Finally, after the vulcanisation and after the wrap and eventually the cord have been removed, the hose is pulled off the mandrel. This pulling off is not as easy as some technologists pretend. Some affirm that this operation can best be done by means of compressed air, which is introduced between the hose and the mandrel by a conical nozzle, but one certainly meets with a difficulty in this connection, as it is impossible for the conical nozzle to loosen the spiral which is tight round the mandrel.

The best method—again of early days!—for facilitating the removal of an armoured hose from the mandrel is to loosen the spiral during the course of fabrication of the hose, so as to prevent its being tight round the mandrel or the canvas. If special attention is paid to this, a few twists will be sufficient for the hose to be loosened and pulled off the mandrel after vulcanisation.

With larger sizes, it is advisable to use sheet tubes, which can be made to spring or be drawn inward.

The mandrels usually employed for the manufacture of all kinds of rubber hoses are smooth-drawn steel tubes, joined by coupling-screws. These tubes are stronger and will last considerably longer than brass mandrels, and, owing to their absolutely smooth surface, a highly varnished inner surface is obtained. Another advantage of steel mandrels, compared with other metal mandrels, is that the rubber does not get baked on firmly. In this respect, however, aluminium mandrels are better still.

Some delivery hoses, as a protection against tear, have naked spirals placed on their outside surface.

Rubber-lined Canvas Hose. Hemp canvas hoses are sometimes made in the rubber factory itself with the aid of special looms, but in most cases they are supplied by textile concerns, the rubber factory having only the task of lining the inside of canvas hose with a layer of rubber. This layer is drawn on the Tubing

Machine, or prepared on the mandrel from a calendered sheet of rubber. The layer is given a preliminary vulcanisation lasting a few minutes. A tape, to draw the rubber is run through the hemp canvas. Then the partially vulcanised rubber tube, well coated with solution, is introduced into it using the above-mentioned tape. The hose is then brought on to a vulcanising cone and firmly clamped on the tube. The other end is connected to the condenser waste pipe, whereupon the vulcanisation is completed by conducting steam through. It is advisable to submit the hose to a steam pressure of about 4 to 5 atm. By the high pressure, the rubber tubing is pressed firmly against the wall of the canvas hose, the solution penetrates the open space, and the fabric and tubing are thus closely addicted. After taking off the pressure, the hose is tested with hydraulic pressure at 20 atm. and then blown through with hot air, in order to dry it well.

Another method for lining the hemp canvas is to apply the solution by means of travelling wires, which, by the aid of rubber brushes attached to them, apply the thick solution evenly to the walls. This method is said to be preferable to the old system described above, as it is supposed to avoid leakages in the tubing, for, when pulling the rubber tubing through, one cannot always avoid drawing it out more than necessary, whereby thin places in the wall are produced.

The old method, however, is to be preferred to the latter, as it is more simple, and, if proper care is taken when pulling the inner tube through the canvas hose, thin places can always be avoided.

Wing-Foot Hoses. These are hoses of a special fabrication 100 to 250 ft. in length, with braided cotton plies and often with striped outer layer. They are employed as delivery hoses, mostly for spraying purposes over wide areas. The inner tube is extruded on the Forcing Machine and talc blown in and then inflated with a little air to prevent the walls from sticking together. The tube is now braided with a layer of cotton threads, and passed through the Tubing Machine having a right angle head. If two plies of braided cotton are required, the hose passes through the braiding machine for the second time and finally through the right angle head of the Tubing Machine for the upper layer of rubber.

Rubber hose thus prepared is covered with lead on the Lead Press used for making armoured cables, the envelope of lead being striped inside to give the same impression to the rubber, after which the hose is vulcanised.

There are two ways of vulcanising such rubber hoses:

(1) By filling the lead covered hose with water under 3½ atm. pressure, and rolling it round a drum to be vulcanised.

(2) The rubber hose with its envelope of lead is connected to a steam pipe, the hose rolled round a drum and vulcanised in that way out of the vulcaniser.

When vulcanised, the lead cover is removed from the hose by means of a special machine having two knives. The rubber hose is passed through this machine, the knives of which cut off the lead from the hose. The rubber hose thus removed from the lead is now ready for despatch.

Passing the hose through the Lead Press is not always cheap, except in factories where manufacture of electrical cables is undertaken, as a Lead Press would cost about a lakh of rupees.

The author, however, suggests another method for making Wing-Foot Hoses:

The inner tube, when extruded on the Forcing Machine, is slightly inflated with air and passed through the Braiding Machine, where, as already explained, one or two layers of cotton yarn are braided on the hose. The hose is then passed through the right angle head of the Tubing Machine provided with a mouth piece capable of giving the required stripes on the outer layer of the hose. Then one end of the hose is tightly closed and the other end attached to a water pipe and water let in at a pressure of 6 to 10 atm. The end connecting the pipe is now closed, and the water-filled hose is rolled round a drum or alternatively placed in talc on a turning table to be vulcanised.

After describing the different methods of making Rubber Hoses of all kinds, the following are the various formulas for rubber compounds to be used in each case:

(1) Rubber Hoses for Vacuum Brakes, Compressed Air, Acetylene, Oxygen etc.

(a)	Smoked sheets	10^{k} 000
	Micronex	2^{k} 500
	Fumonex	1^{k} 000
	Zinc Oxide Active	0^{k} 500
	Ozokerite	0^{k} 120
	Sulphur	0^{k} 250
	Phenylbetanaphthylamine or Anti-oxidant MB	0^{k} 120
	Stearic Acid	0^{k} 150
	Vulkazit F	0^{k} 095

Cure: 25 minutes at 281° F.

(b)	Smoked sheets	10^{k} 000
	Micronex	1^{k} 000
	Kaolin	4^{k} 000

Zinc Oxide Active	0^{k} 500
Ozokerite	0^{k} 120
Sulphur	0^{k} 250
Vulkazit F	0^{k} 095
Acid Stearic	0^{k} 100
Phenylbetanaphthylamine	0^{k} 100

Cure: 20 minutes at 289° F. (143° C.)

(c) *Red.*

Crepe	10^{k} 000
Zinc Oxide Active	0^{k} 600
Silicious Chalk	12^{k} 000
Kaolin	4^{k} 000
Mineral Oil	0^{k} 300
Ozokerite	0^{k} 100
Stearic Acid	0^{k} 075
Vulkazit F	0^{k} 085
Sulphur	0^{k} 220
Iron Oxide 720	0^{k} 500

Cure: 20 minutes at 289° F. (143° C.)

N.B. As already stated in previous chapters, Kaolin, also called China Clay, Geisenheim or Seck, retards the vulcanisation of compounds with Vulkazit F and increases the blooming tendency of the mix. To avoid these troubles, the quantity of accelerator should be slightly increased.

(2) For Steam Hoses.

Smoked sheets	10^{k} 000
Lamp Black Active	2^{k} 000
Zinc Oxide Active	6^{k} 000
Micronex	0^{k} 500
Kaolin	4^{k} 000
Aldolal Powder	0^{k} 150
Phenylbetanaphthylamine	0^{k} 100
Stearic Acid	0^{k} 100

Sulphur	0^{k} 120
Vulkazit F	0^{k} 150
Paraffin Wax	0^{k} 150

Cure: 15 minutes at 289° F. (143° C.)

The solution for rubberising the fabric for insertion in the above hose is made as follows:—

Sheets well masticated	10^{k} 000
Sulphur	0^{k} 240
Zinc Oxide Active	1^{k} 000
Stearic Acid	0^{k} 080
Rosin	0^{k} 100
Mineral Oil	0^{k} 200
Phenylbetanaphthylamine	0^{k} 100
Vulkazit F	0^{k} 085

Another mix for the same purposes with Rubberine-Gel:

Smoked Sheets	5^{k} 200
Sulphur	0^{k} 200
Rubberine-Gel	0^{k} 100
Zinc Oxide	1^{k} 100
Litharge	0^{k} 300
Silicious Chalk	3^{k} 200

Cure: 25 minutes at 140° C.

(3) For Water Hoses.

Smoked Sheets	10^{k} 000
Silicious Chalk	12^{k} 000
Kaolin	4^{k} 000
Vulkazit F	0^{k} 085
Zinc Oxide Active	0^{k} 500
Mineral Oil	0^{k} 300
Paraffin Oil	0^{k} 100
Sulphur	0^{k} 220
Stearic Acid	0^{k} 040

Cure: 20 minutes at 289° F. (143° C.)

(4) For Wine and Beer Hoses:

(a) *Mix for* Inner Tube.

Crepe	10^k 000
Sulphur	0^k 280
Vulkazit 1000	0^k 100
Vulkazit Mercapto	0^k 006
Stearic Acid	0^k 060
Zinc Oxide Special ...	0^k 300
Paraffin Wax	0^k 060
Paraffin Oil	0^k 150
Aldolal Powder ...	0^k 030
Lithopone	0^k 200
Vulcan Fast Orange GF	0^k 200
Vulcan Red BF	0^k 080

(b) Solution for rubberising the fabric for these hoses:

Crepe well masticated	10^k 000
Sulphur	0^k 280
Vulkazit 1000	0^k 100
Vulkazit Mercapto	0^k 006
Stearic Acid	0^k 060
Zinc Oxide Special	0^k 400
Aldolal Powder	0^k 030
Lithopone	7^k 000
Mineral Oil	0^k 400
Wool Grease	0^k 200

(c) Mix for the top layer:

Crepe	10^k 000
Sulphur	0^k 270
Vulkazit 1000	0^k 100
Vulkazit Mercapto	0^k 006
Zinc Oxide Special	0^k 500
Stearic Acid	0^k 060
Paraffin Wax	0^k 080
Aldolal Powder	0^k 030

Lithopone	1^{k} 000
Silicious Chalk	5^{k} 000
Mineral Oil	0^{k} 200
Vulcan Fast Orange GF	0^{k} 100
Vulcan Red LCF	0^{k} 200

Cure: 25 to 35 Minutes at 147° C. (297° F.)

(5) Hoses For Welding Apparatus, Flame Proof.

(a) For inner tube and the solution for rubberising the fabric for insertion:

Smoked Sheets	10^{k} 000
Arubren	10^{k} 000
Magnesium Carbonate	10^{k} 000
Kaolin	2^{k} 000
Zinc Oxide	1^{k} 000
Stearic Acid	0^{k} 100
Sulphur	0^{k} 300
Vulkazit F	0^{k} 300
Aldolalphanaphthylamine	0^{k} 150

(b) For the top layer:

Crepe	10^{k} 000
Arubren	10^{k} 000
Magnesium Carbonate	10^{k} 000
Kaolin	2^{k} 000
Zinc Oxide	0^{k} 750
Sulphur	0^{k} 300
Vulkazit F	0^{k} 300
Aldolalphanaphthylamine	0^{k} 100
Stearic Acid	0^{k} 080

Cure: 25 minutes at 134° C. (274° F.)

Arubren, of which mention is made in the above mixes, is a light-coloured material possessing a faint aromatic odour. At room temperature, it is a semi-solid and somewhat plastic product. It does not show a sharp melting point, but is soft at about 40° C. and a very viscous liquid at about 80° C.

Mixes containing approximately equal proportions of rubber and Arubren, together with suitable fillers, *yield rubber goods which burn only with difficulty.* Such stocks are much more difficult to ignite in an open flame than ordinary rubber, and are extinguished as soon as the flame is removed. No difficulty is experienced in working this material. The rubber is masticated on the rolls rather less than usual, and the Arubren milled in gradually in pieces about the size of the first. Owing to the high Arubren content, the mixes are rather softer than usual; therefore the calender rolls and forcing machine temperatures should be kept fairly low.

The influence of the individual fillers on the inflamability of the mixes varies considerably.

Of the inorganic compounding ingredients, Magnesium Carbonate, Kaolin and Silicious Chalk are especially suitable, but Whiting is not suitable in this case. Magnesium Carbonate yields snappy, elastic vulcanisates with good tensile strength. Kaolin and Silicious Chalk give softer products with rather lower tensiles. Vulcanisates containing Silicious Chalk are outstanding because of their high elasticity.

If gas blacks are to be used with Arubren, it should be noted that active blacks yield vulcanisates of lower elasticity than do inactive blacks. If good wearing resistance is desired, it will be found best to use a combination of both types of black. Gas black, being an organic substance, does not improve the flame resistance of the mix in the same way as inorganic fillers. It is therefore suggested only to use Gas Black as an ingredient in mixes which chiefly contain inorganic substances.

Vulkazit F has proved to be a very useful accelerator for mixes with Arubren, and 2.5 to 3 parts

Vulkazit F are necessary to 100 parts of rubber plus 100 parts of Arubren.

If anti-oxidants are present, a small decrease in tensile values will be noticed both in hot air at 70° C. and also in the Bierer-Davis Oxygen Bomb at 60° C.

The following are the characteristics of some fillers with Arubren, after withdrawal from the flame:

Whiting	burns on.
Kaolin	extinguishes immediately.
Silicious Chalk	extinguishes after two seconds.
Magnesium Carbonate	extinguishes immediately.
Inactive Black	extinguishes after 2 seconds, but glows afterwards and sometimes burns on.
Active Black	extinguishes after 3 seconds, but glows afterwards.

What has been stated above with reference to Arubren was communicated to the author by the Farben Industry in 1935, and after personal trials it has been found that this product is an effective flameproof product.

(6) Mix for Acid and Vinegar Proof Hoses.

Sheets	....	10k 000
Mineral Rubber	....	1k 600
Sulphate of Barium, or Silicious Chalk		3k 000
Zinc Oxide	....	0k 500
Ozokerite or Paraffin Wax	....	0k 100
Stearic Acid	....	0k 050
Aldolal Powder	....	0k 050

Sulphur	0^{k} 240
Vulkazit F	0^{k} 100

Cure: 25 to 30 minutes at 134° C. or
3 to 10 minutes at 151° C.

The hardness of the stock may be increased by adding more Kaolin. Acid-soluble fillers such as Chalk, Magnesium Carbonate and the like cannot be used for this purpose.

If stocks are to be unaffected by edible vinegar, Vulkazit P extra N must be used instead of Vulkazit F, which in any case should not be used for rubber articles coming into contact with foodstuffs.

(7) Mixes for Acetylene Hoses:

(a)	Rubber	10^{k} 000
	Active Gas Soot Micronex	3^{k} 000
	Oil Soot (elastic)	1^{k} 000
	Reclaim ...	2^{k} 500
	Zinc Oxide	1^{k} 500
	Stearic Acid	0^{k} 200
	Ozokerite or Paraffin Wax	0^{k} 100
	Mineral Rubber	0^{k} 600
	Aldolal Power	0^{k} 150
	Sulphur	0^{k} 300
	Vulkazit F	0^{k} 110

Cure: about 30 minutes at 138° C.

(b) *Solution for proofing the fabric for the above* (to be frictioned on the calender.)

As explained in connection with frictioning on the calender, rubber must be well masticated twice, at an interval of 24 hours before being incorporated in the mix.

Sheets	....	10k 000	
Sulphur	....	0k 200	
Zinc Oxide	....	1k 000	
Silicious Chalk	....	2k 500	
Stearic Acid	....	0k 050	
Vulkazit F	...	0k 100	
Rosin	....	0k 050	
Mineral Oil	....	0k 500	(when tetraline is available, a few drops will suffice).
Aldolal Powder	....	0k 100	

When the mix is ready it should be allowed to stand for another 24 hours.

Aldolalphanaphthylamine Powder should always be added in the mix as soon as the rubber is masticated and the fillers have been incorporated.

To facilitate the incorporation of Carbon Black in the mixes, a *master-batch* should be made up as follows:-

The Carbon Black, together with Ozokerite and Mineral Rubber, are mixed with, say, 3 kilos of rubber from 7 (a), and when the Carbon Black thoroughly combines with the rubber, the mix is incorporated in the remaining rubber and fillers.

(8) Petrol-proof stocks for Tanking Hose Pipes:

Natural rubber stocks have only a limited resistance to *petrol and oil* and are frequently insufficient for practical requirements, while the grades from *Synthetic Rubber*, such as the one called Product L, are superior in that respect.

The mix is to be made as follows:-

Product L	....	8k 500
Smoked Sheets	....	1k 500
Inactive Gas Soot P 33		3k 500
Cycline Oil	....	0k 500
Zinc Oxide	....	1k 000
Vulkazit F	....	0k 040

Cure: 20 minutes at 290° F.

Partial Petrol resisting hoses from Natural Rubber are made as follows:

(a) *Inner Tube:*

Smoked Sheets	5^{k} 000
Crepe	5^{k} 000
Silicious Chalk	10^{k} 000
Oil Soot P 33	4^{k} 000
Sulphur	0^{k} 350
Aldolal Powder	0^{k} 100
Vulkazit F	0^{k} 100
Stearic Acid	0^{k} 100
Mineral Oil	0^{k} 150
Paraffin Wax	0^{k} 100
Zinc White	0^{k} 500

(b) *Solution for proofing the fabric for insertion:*

Smoked Sheets well masticated	5^{k} 000
Crepe well masticated	5^{k} 000
Silicious Chalk	8^{k} 000
Oil Soot P 33	0^{k} 500
Sulphur	0^{k} 300
Aldolal Powder	0^{k} 100
Vulkazit F	0^{k} 100
Stearic Acid	0^{k} 100
Mineral Oil	0^{k} 250
Zinc White	0^{k} 500

(c) *Upper layer:*

Smoked Sheets	5^{k} 000
Crepe	5^{k} 000
Silicious Chalk	10^{k} 000
Sulphur	0^{k} 300
Aldolal Powder	0^{k} 050
Vulkazit F	0^{k} 100
Stearic Acid	0^{k} 100
Mineral Oil	0^{k} 150
Paraffin Wax	0^{k} 100
Zinc White	0^{k} 500
Iron Red Oxide 720	0^{k} 600

Cure: 30 to 35 minutes at 272° F.

CHAPTER V.

Manufacture of Extruded Goods.

EXTRUDED goods are produced on the Forcing Machine, also called the Tubing Machine or Extruding Machine. A great variety of goods can be produced on these machines. Their construction is very simple, consisting of a heatable cylinder within which are a revolving worm, also called *Forcing Screw*, and a head with a mouth piece or nozzle with a mandrel inside. The diameter of the mandrel is the same as the inner diameter of the tubing to be manufactured, whereas the die or mouth piece, which is kept in position by set-screws, is of the outer diameter of the goods to be produced.

If worked without the mandrel, the machine produces plain articles either circular or angular, according to the shape of the mouth piece used.

The Tubing Machine works in a simple way. Warmed strips of rubber mix are introduced into the heated cylinder, through a hopper located at the top of the cylinder, inside which they are forced towards the mouth piece by the revolving forcing screw. German makers like Berstorff suggest feeding the machine by means of a pair of rollers instead of through a hopper. By such a system not only is the rubber unnecessarily kneaded, but also the so called *automatic feed* demands the careful attention of the workman in charge just as much as if he were feeding the machine by hand.

As regards their construction, Forcing Machines with short cylinders and strong forcing screws of adequate depth are always preferable in order to ensure suitable pressure.

To obtain a smooth surface it is necessary to heat the machine to a greater or lesser degree according to the quality of the compound to be worked up. Whether the heating is to be confined to the cylinder or to the head of the machine depends entirely on the kind of mixture to be processed. Often it is only the mouth piece which is warmed by a gas flame, by steam, or, more simply by a blow lamp. The extruded article runs on to a galvanised plate covered with talc pivoted in front of the machine, and is then vulcanised.

Forcing Machines are provided now-a-days with *talcum devices* from which compressed air is blown to the talc container through a pipe of ½" diameter. The talc container is connected to the head of the machine by a pipe of ⅜ inch internal diameter. The blown talc is introduced into the mandrel fixed in the head of the machine and from there enters the extruded tubing. The blowing in of talc is to prevent the inner walls of the tubing from sticking together, which would spoil the article. Experience shows that tubings into which air has been blown with talc are often oval in shape, whereas those made of the same composition, but into which air has not blown in talc are perfectly round after cure. This flattening is caused by the introduction of air blowing in talc, but the talc device is a necessity, when bicycle or motor car tubes (the fabrication of which will be discussed in the following Chapters) are produced, and also in the case of inner tubes for hoses, as has been explained in Chapter IV.

The production of tubings with coloured stripes is now very common. This is done on the Forcing Machine with a special head. Such heads are provided with bores, the number of which corresponds to the number of coloured stripes required on the outer surface of the tubing. These bores are filled by hand with the coloured rubber and then fitted on to the machine, and whilst the tubing is extruded from the mouth piece, the rubber inside the cylinder, forced forward by the screw, exerts a pressure upon the coloured rubber in the bores, which then come out in stripes on the tubing. When the bores become empty, the machine has to be stopped to remove the head, the bores of which will have to be cleaned before being refilled to proceed further with the work. By this method only relatively short length tubings can be produced at a time, and the trouble incurred in producing such tubings do not justify such manufacture on any large scale.

Another method for producing tubings with coloured stripes is by employing the J. L. Mahoney's type of forcing machine (American Patent specification 817,080). In this machine, the inner forcing screw working the main compound is encircled by an outer concentric forcing screw, which conveys the colouring compound into a nozzle and presses it on to the tubing in the form of coloured threads.

Garry and Rickshaw Tyres. These are also produced on the Forcing Machine. If the mouth piece is made of the correct dimensions, it is possible to produce these tyres for vulcanisation in open steam either on a round galvanised plate in talc or rolled round a drum. By this method a rather large production can be obtained. Otherwise, after being extruded, these tyres are moulded and vulcanised in the Vulcanising Press.

Perambulator Tyres with or without an inside wire are also produced on the Forcing Machine. For making these with inside wire, a Forcing Machine with a hollow screw or a hollow right angle head is required.

When extruded, they are vulcanised in talc on a galvanised plate, or rolled round a drum.

Air Bags for the manufacture of tyres are produced on the Forcing Machine. They are then moulded and vulcanised in the Watch Case, which is described in Chapter VII.

Gas Tubings, *Valve Tubes* and the like are produced on the Forcing Machine and then vulcanised in open steam in talc. It is not necessary to blow in talc before vulcanisation.

Surgical Tubings are also produced in the same way, but in short lengths, say 5 to 6 ft. These tubings are often produced with stripes, which are obtained by passing the tube through a mouth piece having a serrated inner surface. As a rule, these tubings have rolled ends, which are obtained by introducing into the tubing at either end a small round stick, that part of the tubing having been dusted with talc. The ends are then rolled by hand, and the tube is vulcanised. As in the case of gas tubing, it is not necessary to blow in talc before vulcanisation.

Soda Water Bottle Rings. These are extruded on the Tubing Machine, then they are put on mandrels, perferably of glass, and vulcanised in water without being wrapped, after which they are cut to the required size on a cutting machine. These rings are often red inside with an external white surface, which is obtained by dipping the vulcanised tubing in a self-vulcanising white solution. When the latter is well dried, the tube is cut into rings.

Pedal and Brake Rubbers. These are for the most part drawn on the Forcing Machine in plain cords, corresponding in shape to the respective die, vulcanised in talc and then cut to the required size. If moulded, they can be given any shape and reproduce any design engraved in the mould.

As regards curved brake-rubbers, with an inner layer of hard rubber, called ebonite, when the two compounds have been drawn on the Forcing Machine, the ebonite is affixed to the softer rubber with a solution. The whole thing is then cut to the required size and cured in talc.

The following are formulas, worked by the author for years, which will no doubt be of interest to the Rubber Manufacturer:

Mixes for Gas Tubings:

A White.

Pale Crepe	10^{k} 000
Factice Gloria	2^{k} 500
Carbonate of Magnesia	1^{k} 200
Zinc Oxide Active	0^{k} 500
Vulcan Fast Orange GF	0^{k} 240
Vulcan Fast Red BF	0^{k} 080
Lithopone	0^{k} 250
Ozokerite	0^{k} 100
Sulphur	0^{k} 250
Stearic Acid	0^{k} 050
Cadmium Red GG	0^{k} 050
Vulkazit F	0^{k} 100

B Red.

Pale Crepe	10^{k} 000
Gloria Factice	2^{k} 500
Carbonate of Magnesium	1^{k} 200
Zinc Oxide Active	0^{k} 500
Ozokerite	0^{k} 100
Sulphur	0^{k} 250
Stearic Acid	0^{k} 050
Cadmium Red GG	0^{k} 050
Cadmium Red B	0^{k} 070
Vulkazit F	0^{k} 100

C Black.

Smoked Sheets	10^{k} 000
Brown Factice	3^{k} 000
Carbonate of Magnesia	1^{k} 000
Zinc Oxide	0^{k} 500
Micronex	0^{k} 750
Ozokerite	0^{k} 100
Sulphur	0^{k} 250
Stearic Acid	0^{k} 060
Vulkazit F	0^{k} 100

D Blue.

Pale Crepe	10^{k} 000
Gloria Factice	2^{k} 500
Carbonate of Magnesia	1^{k} 000
Kaolin	3^{k} 000
Silicious Chalk	3^{k} 000
Lithopone	0^{k} 150
Zinc Oxide Active	0^{k} 500
Ozokerite	0^{k} 080
Stearic Acid	0^{k} 050
Sulphur	0^{k} 230
Vulkazit F	0^{k} 100
Vulcan Fast Blue GGF	0^{k} 080

The above four mixes should be cured in talc 8 minutes at 147° C. plus 20 minutes at 138° C.

E Another Mix for White Gas Tubing.

Pale Crepe	10^{k} 000
Kaolin	4^{k} 000
Silicious Chalk	2^{k} 000
Stearic Acid	0^{k} 120
Ozokerite	0^{k} 100
Zinc Oxide Active	1^{k} 000
Sulphur	0^{k} 220

Vulkazit F	0^{k} 120
Lithopone	2^{k} 400

Cure in talc rising quickly up to 147° C. and maintain for 8 minutes, then reduce the temperature to 138° C. and maintain for 20 minutes.

F Another Mix for Black Gas Tubing.

Smoked Sheets	10^{k} 000
Brown Factice	0^{k} 600
Acid Stearic	0^{k} 250
Ozokerite	0^{k} 100
Zinc Oxide Special	0^{k} 600
Sulphur	0^{k} 240
Vulkazit F	0^{k} 100
Arrow Black	4^{k} 000
Mineral Rubber	0^{k} 500

Cure in talc: rising quickly up to 147° C. and maintain for 8 minutes, then reduce the temperature to 138° C. and maintain for 25 minutes.

Mixes for Perambulator Tyres:

A.	Pale Crepe	10^{k} 000
	Sulphur	0^{k} 240
	Vulkazit F	0^{k} 090
	Lithopone	1^{k} 000
	Zinc Oxide	0^{k} 600
	Paraffin Wax	0^{k} 150
	Stearic Acid	0^{k} 060
	Carbonate of Magnesia	1^{k} 500
	Silicious Chalk	21^{k} 500
B.	Smoked sheets	10^{k} 000
	Sulphur	0^{k} 240
	Vulkazit F	0^{k} 090
	Lithopone	0^{k} 200
	Zinc Oxide	0^{k} 600

	Paraffin Wax	0^{k} 150
	Carbonate of Magnesia	2^{k} 000
	Silicious Chalk	21^{k} 500
	Arrow Black	0^{k} 030
	Stearic Acid	0^{k} 060
C.	Smoked Sheets	10^{k} 000
	Sulphur	0^{k} 460
	Vulkazit F	0^{k} 042
	Zinc Oxide	0^{k} 600
	Paraffin Wax	0^{k} 150
	Stearic Acid	0^{k} 060
	Carbonate of Magnesia	1^{k} 000
	Silicious Chalk	21^{k} 500
	Arrow Black	0^{k} 100

Cure of the above three mixes:
30 to 35 minutes at 143° C.

Mixes for Air Bags:

A.	Smoked Sheets	10^{k} 000
	Arrow Black	2^{k} 000
	Zinc Oxide	6^{k} 000
	Micronex	0^{k} 500
	Kaolin	4^{k} 000
	Phenylbetanaphthylamine	0^{k} 100
	Aldolal Powder	0^{k} 150
	Stearic Acid	0^{k} 100
	Sulphur	0^{k} 120
	Vulkazit F	0^{k} 150
	Paraffin Wax	1^{k} 150

Cure in Watch Case mould: 8 minutes at 151° C.

B.	Smoked sheets	5^{k} 200
	Sulphur	0^{k} 200
	Rubberine-Gel	0^{k} 100
	Zinc Oxide	1^{k} 100
	Litharge	0^{k} 300
	Silicious Chalk	3^{k} 200

Cure in Watch Case mould: 25 minutes at 140° C.

C.	Smoked Sheets	10^{k} 000
	Sulphur	0^{k} 400
	Rubberine-Gel	0^{k} 200
	Zinc Oxide	2^{k} 100
	Antimox	0^{k} 200
	Litharge	0^{k} 600
	Carbon Black Thermax	4^{k} 000

Cure in Watch Case mould: 25 minutes at 140° C.

D.	Smoked Sheets	2^{k} 000
	H' Rubber	0^{k} 115
	Sulphur	0^{k} 1015
	Mineral Rubber	0^{k} 2325
	Phenylbetanaphthylamine	0^{k} 060
	Zinc Oxide	0^{k} 500
	Kaolin	1^{k} 500
	Oil Soot Elastic	0^{k} 491

Cure in Watch Case mould: 30 minutes at 141° C.

N. B. The H' Rubber is made up of:

Crepe	9^{k} 000
Vulkazit H	1^{k} 000

Mix for Valve Tubing:

Pale Crepe	10^{k} 000
Zinc Oxide Active	0^{k} 100
Stearic Acid	0^{k} 100
Ozokerite	0^{k} 060
Paraffin Oil	0^{k} 150
Vulkazit P extra N	0^{k} 032
Vulkazit DM	0^{k} 006
Vulkazit Thiuram	0^{k} 006
Sulphur	0^{k} 240
Anti Oxidant MB	0^{k} 030
Magnesium Carbonate	0^{k} 400

Cure in talc: 20 minutes at 132.8° C.

Mix for Surgical Tubing:

Pale Crepe	10^k 000
Zinc Oxide Active	0^k 100
Stearic Acid	0^k 100
Ozokerite	0^k 060
Paraffin Oil	0^k 200
Sulphur	0^k 240
Vulkazit P extra N	0^k 030
Vulkazit DM	0^k 008
Vulkazit Thiuram	0^k 008

Cure in talc: 6 minutes at 143° C. plus 15 minutes at 126° C.

In the foregoing mixes only Vulkazit F has been indicated as an accelerator. It is to be understood that Ureka White F and the Takars can be used instead.

The following datas are to be observed for obtaining round tubings, free from deformation.

Short working of the stock on the mixing rollers; avoidance of too great plasticising; extruding of stocks on the Tubing Machine at the lowest possible temperature consistent with the obtaining of a good smooth surface; and curing of tubings with the shortest possible rise.

The time for working the mixes on the Mixing Rollers should not exceed 40 minutes. To obtain a better dispersion of the accelerator in the compound, factice is first to be incorporated in the rubber, then stearic acid, and then the remaining chemicals in which Vulkazit F has been mixed.

When the mixes are extruded on the Forcing Machine, the cylindric body as well as the head should be kept cold, the mouth piece being warmed preferably by a blow lamp, only just enough to give the tubings a smooth surface. For vulcanisation, the temperature should not vary and it is essential to reach the maximum temperature of 147° C. as quickly as possible, so as to prevent the tubings becoming flat.

CHAPTER VI.

The Manufacture of Inner Tubes.

SINCE about the year 1925, automobile manufacturers have been producing wheels of smaller and smaller size, and it was about the same year that the so called *Balloon Tyres* first made their appearance. These two innovations brought to the rubber manufacturers the problem of making *inner tubes* of a shape to fit properly into the new tyres. It may be stated that up to that time the bulk of inner tube production was by vulcanising on straight mandrels, and tubes made on circular mandrels were an exception. Large truck and bus tubes of 6 inch diamater and more, however, were frequently vulcanised in moulds until about 1925. For this purpose, they were introduced into a tyre vulcaniser or Watch Case in much the same way as air bag moulds. Carbon dioxide or nitrogen, or some other inert gas was necessarily used for internal pressure, and since heated air under pressure for the length of time these tubes were cured would give an oxidised and sticky inside surface, some manufacturers of those days only used to half-cure these large tubes on straight or curved mandrels and then vulcanise the splice and shape the tubes in air bag moulds.

Another method of producing these larger tubes was to use circular mandrels, and as far as vulcanisation was concerned, this method was not different from that in which straight poles were used. Up to the advent of quick-acting individual moulds, most of the larger sizes of balloon tubes had been made by this circular mandrel method.

Since then, various types of individually heated moulds have been introduced, and have all been favourably received. They all operate on the same principle. Each provides a tube cavity, heated directly by steam in an adjacent jacket. In some types, the jacket is cast integrally with the mould, whereas in others the mould is attached to the jacket. The primary difference is in the manner of operating the mould and of opening up the cavity for the removal of a cured tube and the insertion of an uncured one. Further differences are apparent in the method of locking the mould during vulcanisation period. Whatever that method may be, it should be remembered that any equipment designed to provide uniform heating, rapid changing and fine seam marks, should be satisfactory, as it is admitted that the ability to make quick changes is a vital item, since local heating of the uncured stock will cause thin spots on expansion, and consequently poor tubes.

We know that in America, the bulk of the inner tube production for many years has been made by the individual mould method, and we know also that in Europe, where the bulk of the production has been made by the circular mandrel method, the individual mould is now more and more used. The reason for this is the fact that in America labour is expensive and machinery relatively cheap, whereas in Europe the reverse is the case. This accounts for the slow changing over from circular mandrels to moulds in the case of European factories, while factories in America were forced to adopt the individual moulds immediately after their introduction.

In early days tubes were made in America from calendered sheets, which were in two-ply, rolled twice round a straight pole preferably in one operation, and then vulcanised without wraps either in water or in open steam.

In Europe, the general method of tube production has been by extruding the stock from a Tubing Machine and then blowing the tubes either on straight or curved mandrels. In fact this method was used in America, specially for larger size tubes, but there, on account of the high labour cost, the calendering method is cheaper for volume production. This remark applies only to the use of straight mandrels. Whatever it be, the tubed stock has a definitely lower labour cost and a further advantage of readily permitting a cure without wraps or other external pressure, as there is no longitudinal seam to be forced to flow down.

Stock to be tubed naturally has to be compounded in such a manner as to permit the free flow from the machine at a speed which will give reasonable capacity. The stock must also flow quite smoothly, as irregularities in gauge are fatal during the expansion process, and any slight irregularity at this stage would magnify itself many times later. Talcum is blown into the interior surface of the stock, as it is tubed, to prevent sticking, and this is very carefully cleaned off, when the ends are spliced, in order to obtain a perfect union. There are methods of obtaining a fairly uniform gauge when tubing stocks: by setting the centre pin somewhat off centre, the gauge from one side to the other can be varied at will, and by making the thinner gauge on the inside or valve side, a fairly uniform thickness is obtained after the tube is spliced and inflated.

The outstanding feature, as has been mentioned before, of the operation of moulded tube equipment is the speed with which tubes may be changed. It seems that the factory success of the moulding of the tube depends quite largely upon the time taken between the insertion of the tube in the hot mould and the expansion of the stock to the closed mould. If the stock is expanded before it has a chance to heat up, then no thinning out is encountered. If, however, the stock warms up in spots, then trouble will be had with thin places on the finished tube.

Naturally the financial success of individual mould equipment for tubes depends quite largely on the time of cure of the stocks chosen, and the method would not be economical if one or two-hour cures were required to vulcanise the tube. What we want at the present time is a stock that will cure as rapidly as possible and yet have a uniform cure throughout and at the same time permit of a well cured valve patch. One must remember that heat is applied to the stock from one side only, and that there is air under relatively high pressure on the other side. Prolonged contact with air under high temperature and pressure will cause the inside of the tube to become badly oxidized. It is then necessary in cures longer than a few minutes to use some inert gas such as carbon dioxide or nitrogen, which will not attack the rubber. This is expensive, so when a short cure can be used, one not only saves expense by quicker turnover of the equipment, but also eliminates the cost of using these other gases. It is found that for cures up to about 10 minutes, the oxidation caused by using air is so small as to be negligible.

When we think of quick cures of from 5 to 10 minutes, we naturally first think of ultra-accelerators, as we all know that rapid cures are only possible with these materials. But we all know also that satisfactory results with ultra-accelerators are not obtained with short cures at the higher temperatures and that the real properties of these super-accelerators are brought out only when we vulcanise for a relatively longer period of time at a much reduced temperature. So, the ultra-accelerators so far known give their best properties when used at a temperature varying from 120 to 125° C. and under these circumstances it requires from 12 minutes upwards to vulcanise a small size moulded tube. On using this class of accelerators at higher temperatures, we obtain a very sharp peak in our cure, and from this point onwards usually get a rapid depolymerisation or reversion of the stress strain curve, and we can affirm without exaggeration that we start to reclaim the outside of the tubes before the inside becomes vulcanised!

The difficulty in using ultra-accelerators is that pre-vulcanisation is very difficult to avoid. Most of these accelerators cause vulcanisation of the stock when about or slightly above room temperature. Further difficulties are encountered in preventing scorching of the stock during milling and tubing operation as well as in re-handling the scrap from the tubing machine and building operations. These are difficulties which exist even at present.

What has been said above regarding inner tubes relates to the manufacture of motor car tubes. The same principles and the same process can equally well be employed for the manufacture of bicycle tubes.

Extruding the tubes from the Forcing Machine and having them moulded in the quickest possible manner is no doubt the surest way to success. For this purpose, the author has disigned a combination of moulds. He intended to have this made in Europe just before the outbreak of the present War. He feels certain that the results which can be obtained with these moulds will be extremely satisfactory. The working process of the contrivance is as follows:—

Six moulds are made to run over a circular rail by means of electrically driven wheels. Only one man is required to operate the six moulds. The speed at which the moulds move over the rails will be governed by the time required for the cure, so that one circuit over the rails will have cured the tube. The moulds automatically open and shut when they reach a certain point during their circuit, giving the workman in charge just enough time, say a minute or so, to insert the tube to be vulcanised. When one mould is thus dealt with, it moves to the other side, and the next one occupies its position, and is dealt with in the same way. The same procedure is adopted with regard to the rest of the moulds, and when each of the moulds re-appear, say after six minutes or so, i. e. the time required for vulcanising, the tube is removed from the mould and is ready for despatch, the valve having already been placed on it before its cure.

This is the method by which the author intends to produce moulded inner bicycle tubes.

In the meantime, bicycle tubes are produced by the employment of another method, which, although it gives complete satisfaction, takes a longer time. For the exploitation of this method, we use a forcing machine of 80 mm. with a right angle hollow head. The internal small mandrel, the extremity of which is made of fibre, is located in the head of the machine. This mandrel is hollow to allow the naked aluminium mandrel to pass through. The mouth piece of the tubing machine is of the exact size of the external diameter of the tube to be extruded. The cylindric body being cold, the mouth piece is warmed with a blow lamp, and the forcing machine is thus ready to start work. The mix is introduced into the machine through the hopper as explained in chapter V of this part, and the rubber compound with a smooth surface comes out of the mouth piece. Then the aluminium mandrels are engaged in the forcing machine through the right angle hollow head, one mandrel following the other, and successively these mandrels come out of the mouth piece enveloped with a rubber tube of the ruquired thickness of the bicycle tube (see fig. XIII). On an average, 150 tubes can be produced in one hour.

The mandrel with its tube is removed from the conveying table in front of the Forcing Machine and placed in the chariot of the vulcaniser (see fig. XVI), where the valve patch previously made ready, is fixed upon the outer surface of the tube. The tube without wrapping is now ready to be vulcanised. After cure, the tube is removed from the mandrel. This is a somewhat difficult task. Makers like Berstorff suggest the insertion of valves with flattened mouth pieces between the vulcanised tube and the mandrel and claim the easy removal of the tube from the mandrel by blowing in compressed air through these valves. This method is in actual fact not so easy, and much precious time will be wasted for removing 450 tubes vulcanised in one batch from the 450 mandrels.

We have designed a simple device for removing these tubes, (see fig. XXII).

A certain number of galvanised pipes are connected to a compressed air tank. The mandrels with their tubes are introduced into these galvanised pipes, the end of the rubber tube is forced upon the entrance of the galvanised pipe and the opening of the mandrel is closed with a cork. Compressed air is then allowed into the galvanised pipe and, without any affort, the

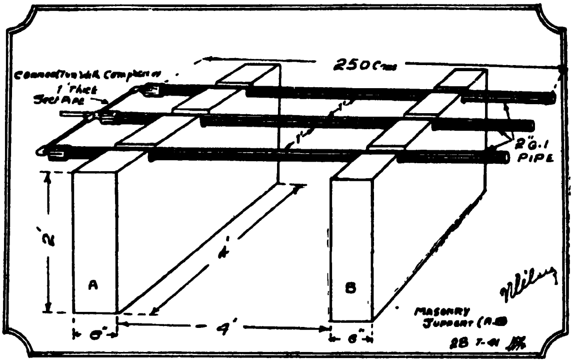


Fig. XXII

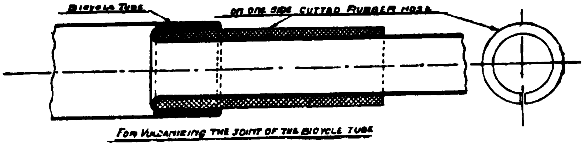


Fig. XXIII.

Fig. XXIV.

aluminium mandrel is pushed forward reversing the tube at the same time, showing the glazed surface which was in contact with the polished aluminium mandrel. Only 20 seconds are necessary to remove the tube from the mandrel, and by having a number of pipes as shown in fig. XXII, 450 tubes can be removed in the course of a few minutes. Then the tubes are cut to the standard lengths, the valve patch punched and the valve fixed immediately afterwards.

Both the ends of the tube are skived, buffed and cemented with a quick-vulcanising solution, jointed and mounted on a piece of rubber hose opened longitudinally on one side (see fig. XXIII). The external diameter of this hose corresponds with the size of the cycle tube. The splice is then vulcanised in an individual vulcanising apparatus (see fig. XXIV).

The following mixes with Vulkazit F have a good deal of Paraffin Wax to prevent the appearance of light spots which often appear when articles containing Vulkazit F are exposed to sunlight.

It is also likely that tubes vulcanised without wraps may show a good many little pits which are caused by vulcanisation in wet steam. In reality, the steam condenses at the start of the cure with the result that drops of water cover the surface of the tubes. To obviate this, it is necessary to reach the required vulcanisation temperature as quickly as possible and to vulcanise with dry steam.

Much worked mixes on the rollers or freshly made mixes are susceptible to steam condensation. To avoid this trouble it is therefore advisable that newly extruded tubes should be allowed to rest for a few hours before being vulcanised. To help the reaching of the fixed vulcanising temperature, stearic acid should be reduced as much as possible, provided this reduction does not hinder the extruding process.

Tubes made with the following mix in 1933, the formula for which was established while the author was in Karachi, are still in very good condition.

V 13.	Pale Crepe	10^{k} 000
	Gloria Factice	0^{k} 800
	Zinc Oxide Special	1^{k} 000
	Sulphur	0^{k} 250
	Paraffin Wax	0^{k} 120
	Cycline Oil	0^{k} 200
	Stearic Acid	0^{k} 050
	Silicious Chalk	3^{k} 000
	Vulkazit F	0^{k} 070
	Vulcan Orange G extra F	0^{k} 070
	Vulcan Red LCF	0^{k} 070

Cure: Rise as quickly as possible to 297° F. and maintain for 12 to 14 minutes at 297° F.

V 14. Non-blooming grey stock:

Smoked Sheets	10^{k} 000
Sulphur	0^{k} 240
Zinc White	0^{k} 800
Cycline Oil	0^{k} 300
Paraffin Wax	0^{k} 100
Silicious Chalk	4^{k} 500
Inactive Carbon Black	0^{k} 010
Stearic Acid	0^{k} 050
Vulkazit F	0^{k} 060

Blooming Grey Stocks:

	V 15.	*V 16.*	*V 17.*
Smoked Sheets	10^{k} 000	10^{k} 000	10^{k} 000
Sulphur	0^{k} 450	0^{k} 450	0^{k} 450
Zinc Oxide	0^{k} 800	0^{k} 800	0^{k} 800
Cycline Oil	0^{k} 300	0^{k} 600	0^{k} 300
Paraffin Wax	0^{k} 100	0^{k} 100	0^{k} 100
Whiting	2^{k} 500	3^{k} 000	2^{k} 500
Silicious Chalk	-	7^{k} 000	-

	V 15.	*V 16.*	*V 17.*
Lithopone	-	-	1k 000
Inactive Carbon Black	0k 010	0k 100	0k 010
Stearic Acid	0k 050	0k 050	0k 050
Vulkazit F	0k 036	0k 036	0k 036

The mixes V 14, V 15, V 16 and V 17 are cured in open steam, the tubes not wrapped, rising as quickly as possible to 143° C. and maintaining for 16 minutes at 143° C.

Two *red* mixes for tubes:

	V 18.	*V 19.*
Pale Crepe	10k 000	10k 000
Paraffin Wax	0k 080	0k 080
Cycline Oil	0k 300	0k 300
Silicious Chalk	3k 000	-
Sulphate of Barium	-	5k 000
Zinc Oxide	0k 800	0k 800
Lithopone	0k 300	0k 300
Sulphur	0k 240	0k 240
Stearic Acid	0k 050	0k 050
Vulkazit F	0k 055	0k 055
Vulcan Fast Orange G	0k 025	0k 025
Vulcan Red L C	0k 075	0k 075

Cure: same as for V 14.

The following is a *Silver Grey* mix for tubes:

V 20.	Smoked Sheets	10k 000
	Sulphur	0k 450
	Zinc Oxide	0k 800
	Paraffin Wax	0k 100
	Cycline Oil	0k 300
	Stearic Acid	0k 050
	Vulkazit F	0k 038
	Lithopone	0k 250
	Carbon Black	0k 010
	Whiting	2k 500

Cure: rise quickly to 147° C. and maintain at 147° C. for 15 to 16 minutes.

Another *red mix* for tubes:

V 21.	Pale Crepe	10^{k} 000
	Zinc Oxide Special	0^{k} 300
	Sulphur	0^{k} 240
	Silicious Chalk	1^{k} 600
	Stearic Acid	0^{k} 050
	Paraffin Wax	0^{k} 080
	Cycline Oil	0^{k} 250
	Vulkazit F	0^{k} 055
	Cadmium Red G	0^{k} 200

Cure: rise quickly to 147° C. and maintain for 14 minutes at 147° C.

The following is a *transparent mix* for tubes:

V 22.	Smoked Sheets	10^{k} 000
	Sulphur	0^{k} 240
	Zinc Oxide Active	0^{k} 080
	Vulkazit F	0^{k} 080

Cure: rise quickly to 142.8° C. and maintain for 10 minutes at 142.8° C.

The following is a tube mix for bus and lorries (heat resisting):

V 23.	Smoked Sheets	10^{k} 000
	Zinc Oxide	0^{k} 500
	Soft Carbon Black	4^{k} 000
	Sulphur	0^{k} 100
	Stearic Acid	0^{k} 100
	Flectol H	0^{k} 200
	Ureka White	0^{k} 200

Cure in open steam: rise quickly to 135° C. and maintain for 30 minutes at 135° C.

Cure in moulds: rise quickly to 147° C. and maintain 10 to 12 minutes for small moulds, and 12 to 18 minutes at 140° C.

A suitable mix for *Motor Car Tubes* is as follows:

V 24.	Crepe	10^{k} 000
	Silicious Chalk ...	3^{k} 000
	Sulphur	0^{k} 200
	Vulkazit F	0^{k} 070
	Paraffin Wax	0^{k} 120
	Vulcan Red LCF	0^{k} 030
	Cycline Oil	0^{k} 200
	Zinc Oxide Special	0^{k} 400
	Phenylbetanaphthylamine	0^{k} 050

The addition of Phenylbetanaphthylamine as an anti-oxidant and fatigue-inhibitor, in spite of the discoloration on exposure to light, is under all the circumstances advisable in the case of motor car tubes which are strained more heavily than cycle tubes.

The cure in open steam of V 24 is 12 minutes at 297° F. Now-a-days motor car tube stocks with a small content of sulphur are preferred as they show excellent *resistance to ageing and heat*, two qualities which are highly desirable.

The following mix is another suitable one:

V 25.	Smoked Sheets	10^{k} 000
	Zinc Oxide Special	1^{k} 000
	Paraffin Wax	0^{k} 100
	Stearic Acid from	0 to 0^{k} 050
	Silicious Chalk	3^{k} 000
	Vulkazit F	0^{k} 125
	Vulkazit 1000	0^{k} 020
	Phenylbetanaphthylamine	0^{k} 060
	Aldolal Powder	0^{k} 060
	Sulphur	0^{k} 110
	Cycline Oil	0^{k} 200
	Vulcan Red LCF	0^{k} 030

Cure: rise quickly at 280° F. and maintain for 12 minutes at 280° F.

Still another, but a *black stock* for motor car tubes is the following:

V 26.	Smoked Sheets	10^{k} 000
	Vulkazit F	0^{k} 150
	Sulphur	0^{k} 100
	Neutral Carbon Black P33	3^{k} 000
	Mineral Rubber	0^{k} 400
	Paraffin Wax	0^{k} 080
	Stearic Acid	0^{k} 100
	Zinc Oxide	1^{k} 000
	Phenylbetanaphthylamine	0^{k} 060
	Aldolal Powder	0^{k} 060

Cure: rise quickly to 280° F. and maintain for 15 minutes at 280° F.

To prove how sulphur can affect the tensile strength, if for instance in V 26, 2.4% of sulphur is added instead of 1%, the tensile strength of that mix, if properly vulcanised, will be reduced by 60%.

The following are mixes for *patches for tube repairs:*

Red V 27.

Crepe	10^{k} 000
Zinc Oxide Special	1^{k} 000
Paraffin Wax	0^{k} 100
Silicious Chalk	3^{k} 000
Vulkazit F	0^{k} 125
Vulkazit Thiuram	0^{k} 120
Phenylbetanaphthylamine	0^{k} 060
Aldolal Powder	0^{k} 060
Sulphur	0^{k} 110
Cycline Oil	0^{k} 200
Vulcan Red LCF	1^{k} 200
Vulcan Fast Orange GF	0^{k} 400

Cure: 4 to 5 minutes at 304° F.

Black V 28.

Smoked Sheets	10^{k} 000
Zinc Oxide Special	1^{k} 000

Paraffin Wax	0^{k} 100
Silicious Chalk	3^{k} 000
Vulkazit F	0^{k} 125
Vulkazit Thiuram	0^{k} 120
Phenylbetanaphthylamine	0^{k} 060
Aldolal Powder	0^{k} 060
Cycline Oil	0^{k} 200
Neutral Carbon Black P 33	0^{k} 300

Cure: 4 to 5 minutes at 304° F.

Below we give *comparative figures of Cycle Inner Tubes of different makers:*

The Singapore Inner Tube 1st quality:

Width of the tube when flat	45	mm.
Length of the tube before joining	2060	,,
Length of the joint	35	,,
(The joints are cold vulcanised)		
Weight of the tube without valve	6½	oz.
Thickness of the wall	1½	mm.

Valve patch with canvas instertion is placed inside the tube.

The Singapore Inner Tube 2nd quality:

Width of the tube when flat	44	mm.
Length of the tube before joining	2070	,,
Length of the joint	35	,,

The Japanese Inner Tube 1st quality:

Width of the tube when flat	45	mm.
Length of the tube before joining	2010	,,
Length of the joint	45	,,

The Japanese Inner Tube 2nd quality:

Width of the tube when flat	45	mm.
Length of the tube before joining	2060	,,
Length of the joint	45	,,

The German Inner Tube:

Width of the tube when flat	40	mm.
Length of the tube before joining	2020	,,
Length of the joint	45	,,

CHAPTER VII.

Manufacture of Bicycle Tyres.

SKILLED hands are necessary for the manufacture of tyres, and in the factory ample space should be provided for that section so that workmen can move about freely without being hindered by machines and working tables. Cleanliness in this particular section is of the utmost importance. Oils and greases should be prohibited, as every fleck of dirt and every spot of oil on the canvas will cause the tyre to be defective in those particular places. The tables should be covered with zinc sheets, the whole surface perfectly even, the end of a zinc sheet soldered to the next one without any overlapping. Washing accommodation should be available in the tyre department so that workmen may clean their hands as often as required.

The canvas* with which the tyre is generally built is a fabric called *tissue-corde,* preferably 140 mm. wide, the warp threads of which are of very strongly twisted cotton yarn, whereas the weft threads are of single cotton yarn, and are used just to tow the warp yarns together.

The canvas is rubberised either with solution on the Rubberising Machine or frictioned on the calender, both the processes as already explained in Part II,

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*Now-a-days United States car tyre manufacturers are now largely replacing canvas by *Rayon,* which is an artificial silk. They have found that *Rayon* is more resistant to wear than cotton, with the result that the tyre mileage is thereby greatly increased. If *Rayon* is used in place of cotton fabric for the building up of cycle tyres, no doubt the life of the latter would also thereby be appreciably prolonged.

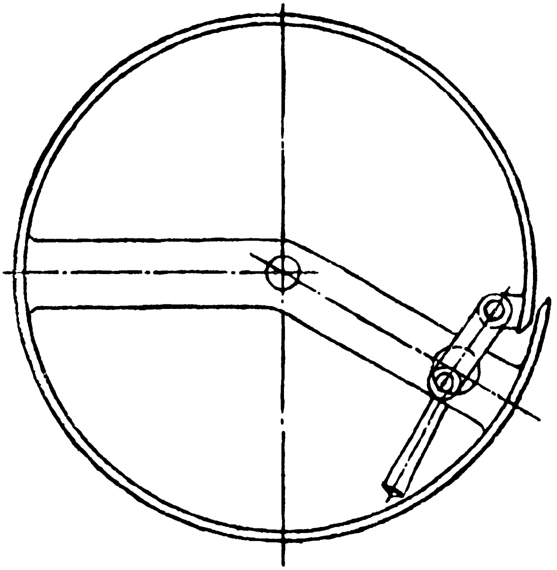


Fig. XXV.

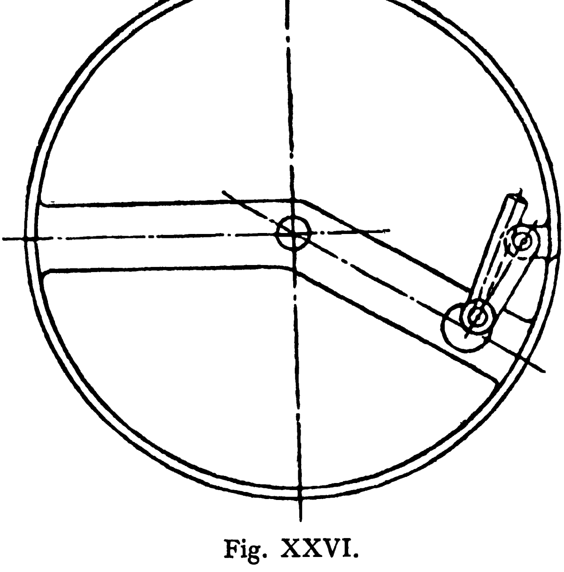


Fig. XXVI.

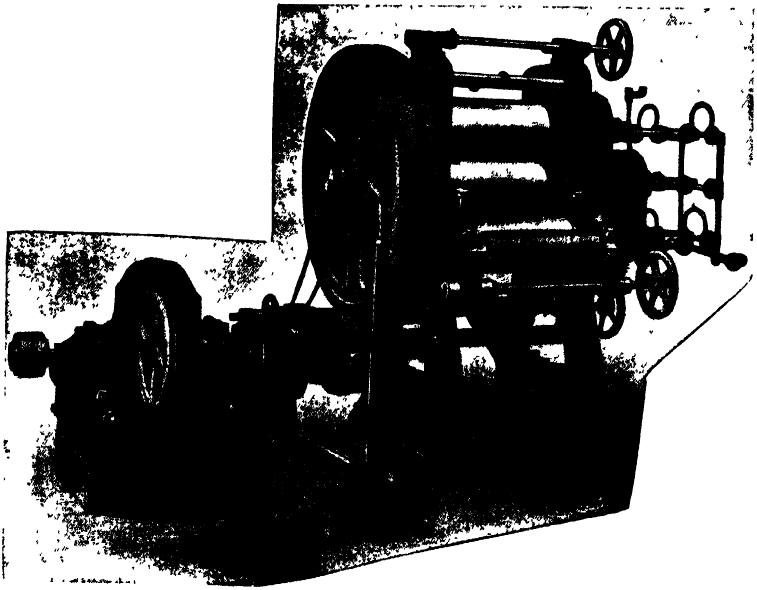


Fig. XXVII.

Chapter III. When the canvas is frictioned on the calender, the fabric shrinks by about 5% of its width.

The carcass of the bicycle tyre is either made from one ply or two plies of the rubberised canvas. For the manufacture of tyres with a single ply—which are the most common—the *tissue-corde* is cut at an angle of 45°, in strips each exactly 182 mm. wide. The length is such that both the ends can join by overlapping slightly so as to make an endless band. It is then put on the collapsed drum (see fig. XXV). Two grommets are now placed on to the canvas in the grooves specially provided on the drum for that purpose.

The grommets for cycle tyres of 28″ x 1½″ are of first class galvanised patent steel of ⅛ mm. diameter wire, with a breaking strain of 140/150 kg. per sq. mm., the inner circumference of the grommets being just 1996 mm.

The grommets can be made in the factory, but care should be taken that the wire should be soldered with a mixture of borax and brass-file-dust.

The collapsed drum is then extended to the utmost so that it is in an absolutely cylindrical form. (see fig. XXVI).

Both sides of the canvas lying outside the grommets are folded so as to join at the centre, one overlapping the other by 6 to 8 mm. In order that the plies may stick well together, the canvas so prepared is pressed by a hand roller.

The whole canvas is then washed with solvent and the rubber protector which is the tread stock of the tyre, drawn on a special profiled calender (see fig. XXVII) in the shape of what is called a *camel back*, is placed upon the canvas and again well rolled with a hand roller, care being taken that air bubbles, if any, are removed with the point of a pin.

As regards the tyre with two plies, they are manufactured by the following method:

The strip of tissue-corde is cut as aforesaid at an angle of 45°, but only 108 mm. wide, and placed round the drum, both the ends joined so as to form an endless band. The drum is then collapsed and both the grommets are fixed on top of the band in the grooves, the sides of the canvas folded over both the wires. Then another strip of tissue-corde of 84 mm. width is placed on top of the first one just between the two wires, the collapsed drum being extended to its full extent and the rubber protector is placed as in the case of the tyre with one ply. Collapsing the drum again the tyre is removed and the air bag is inserted in it.

The air bag is produced on the Tubing Machine with a mouth piece having the required shape of the bag. At the given length the ends of the so called bag are cut at an angle of 45° and before joining them the special valve is inserted in the bag. Care should be taken that the said valve, reinforced with a rubber piece, is well fixed, so that after vulcanisation no air may escape from the closed bag. The air bag is then vulcanised in the special mould adjusted in one of the Watch Cases (see fig. XIV) after which it is ready to be inserted in the tyre for its cure. Preparatory to that cure, the air bag, before being inserted, is well powdered with talc, after which the tyre is given somewhat its proper shape by hand. At this stage the two clip rings are fixed on to the tyre, which is then ready to be introduced into the special mould called Watch Case, wherein the vulcanisation takes place. The watch case is closed partly by hand and compressed air is then allowed to act upon the ring system bayonet, which presses upon the lid of the Watch Case, so that it closes hermetically.

The valve of the air bag is now connected with the air compressor, the pressure of which inflates the air bag which presses the rubber of the tyre against the engraved mould.

Then steam is let into the Watch Case and the cure starts. When the vulcanisation is over, the compressed air is shut off and by reversing the hydraulic pressure, the watch case opens automatically.

The tyre can then be removed from the mould and the cliprings. After trimming the waste, the tyre is powdered with talc and is ready for despatch. The date and the name of the maker, if not engraved on the mould, are sometimes printed inside the canvas. The special ink used for this purpose is made up of the following formula:

Gas Black	about 50%
Oleic Acid	about 50%

Such ink does not attack any rubber compound which contains Zinc Oxide.

It may sometimes happen that the engraved design is not well produced on the outer surface of the tyre owing to the formation of air bubbles in the tread stock during vulcanisation. To avoid this trouble:

(1) allow the compressed air in the air bag to act for half a minute on the tyre before admitting the steam for the cure, then reduce the air pressure for another half minute and finally allow the air pressure to act in full and then start with vulcanisation;

(2) keep the tyre for half a minute in the Watch Case under air pressure and then admit the steam for the cure.

The moulds of the Watch Case should be well covered with mould paste as stated in Part I, Chapter VIII.

A very good cycle tread compound is as follows:

Smoked Sheets	10k 000
Sulphur	0k 322
Rubberine-Gel	0k 678
Zinc Oxide	0k 500
Litharge	0k 500
Carbon Black Arrow	3k 600
Carbon Black P33	1k 800
Mineral Rubber	0k 200

Cure in the Watch Case: 3 minutes at 164° C.

When so vulcanised, the tyre will have a little blooming effect.

If vulcanised in 6 minutes at 164° C. the tube shows no blooming effect and is of a brilliant black shade.

Cure in 3 minutes has certain advantages:

(1) The rubber conserves a good nerve.

(2) The canvas is preserved, otherwise it will be destroyed by prolonged vulcanisation.

(3) It permits of a bigger output.

In conclusion, the Rubberine-Gel can be considered the best activator for litharge, which permits the cure in as short a time as 3 minutes.

Here is a mix for solution to be applied on the Tissue-corde:

Pale Crepe well masticated	10k 000
Sulphur	0k 300
Carbonate of Magnesia	0k 500
Zinc Oxide	0k 500
Vulkazit DM	0k 100

Cure: 7 minutes at 158° C.

The following is a mix for frictioning the tissue-corde on the Calender:

Smoked Sheets	10k 000
Pine Tar	0k 400

Mineral Rubber	1^{k} 000
Rubberine-Gel	0^{k} 100
Captax	0^{k} 100
Vulkazit Thiuram	0^{k} 100
Sulphur	0^{k} 400
Zinc Oxide	0^{k} 500
Carbon Black Arrow	0^{k} 200
Carbon Black Thermax	0^{k} 400
Silicious Chalk	2^{k} 890

Cure: 7 minutes at 158° C.

For this frictioning work the upper cylinder of the calender should be heated to 42° C., the central cylinder to 67° C., and the lower cylinder to 50° C.

The rubber should be masticated as stated in Part II Chapter II.

The following is a mix for Air Bags for extrusion on the Tubing Machine:

Smoked Sheets	10^{k} 000
Stearic Acid ...	0^{k} 400
Phenylbetanaphthylamine	0^{k} 200
Zinc Oxide	10^{k} 000
Heavy Carbonate of Magnesia	0^{k} 200
Kaolin	5^{k} 000
Vulkazit Thiuram	0^{k} 300
Captax	0^{k} 050

Cure: 30 minutes at 141° C.

Red Cycle tread stock:

Pale Crepe	26^{k} 450
Sulphur	1^{k} 015
Zinc Oxide	1^{k} 800
Stearic Acid	0^{k} 250
Paraffin Wax	0^{k} 500
Mercapto GI	1^{k} 500
H' Rubber	0^{k} 250

Titanium White	0^{k} 600
Red Cadmium	0^{k} 600
Silicious Chalk	17^{k} 500

Cure: 7 minutes at 158° C.

The products Mercapto GI and H' Rubber are master-batches composed of 90% raw rubber and 10% accelerator.

Mercapto GI is:

Pale Crepe	9^{k} 000
Vulkazit Mercapto	1^{k} 000

H' Rubber is:

Pale Crepe	9^{k} 000
Vulkazit H	1^{k} 000

Tread stock for tyre with Vulkazit F:

Smoked Sheets	8^{k} 000
Pale Crepe	2^{k} 000
Gas Black	4^{k} 000
Zinc Oxide	1^{k} 000
Pine Tar	0^{k} 150
Stearic Acid	0^{k} 250
Phenylbetanaphthylamine	0^{k} 150
Sulphur	0^{k} 280
Vulkazit F	0^{k} 100

Cure: 20 minutes at 132. 8° C.

Another friction stock for the Calender:

Smoked Sheets (masticated as already stated)	10^{k} 000
Zinc Oxide	1^{k} 500
Pine Tar	0^{k} 300
Stearic Acid	0^{k} 050
Phenylbetanaphthylamine	0^{k} 100
Sulphur	0^{k} 200
Vulkazit F	0^{k} 100

Further Cycle Tread Stocks:

	Black.	*Red.*	*Transparent.*
Smoked Sheets	10k 000	10k 000	10k 000
Sulphur	0k 260	0k 250	0k 250
Zinc Oxide Special	0k 500	0k 600	-
Gas Black	1k 500	-	-
Silicious Chalk	6k 000	6k 000	-
Zinc Oxide Active	-	-	0k 110
Stearic Acid	0k 100	0k 080	0k 080
Cycline Oil	0k 300	0k 300	-
Paraffin Wax	0k 100	0k 080	0k 050
Vulkazit F	0k 110	0k 100	0k 100
Titanium Dioxide	-	0k 100	-
Vulcan Fast Red GF	-	0k 160	-

Cure: 6 minutes at 151° C.

A still shorter cure can be obtained by adding 5 to 10 parts of Magnesium Carbonate, or 0.1 to 0.2% of Vulkazit 1000.

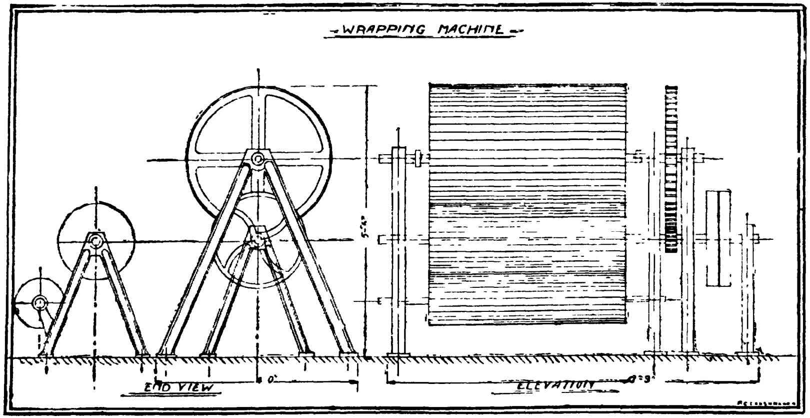
CHAPTER VIII.

Manufacture of Rubber Sheetings.

FOR the manufacture of Rubber Sheetings, which constitute an important branch of the rubber industry, the calendered sheeting and coated fabric for insertion form the basis as a foundation for working upon. Packing sheet with insertion is usually prepared by rolling the layers of rubber on to the coated canvas. The process can be simplified by doubling the coated fabric with the sheet on the calender. The finished sheeting, before being cured is wound up and wrapped on a Wrapping Machine (see fig. XXVIII) between wet fabrics, in order to keep it free from blisters and to firmly attach the insertions to the various layers of rubber during vulcanisation. Packing sheeting may also be press cured, in which case the cost of curing would be somewhat high, but the smooth shining surface obtained by press cure will give the finished articles a nice appearance.

Another method of obtaining sheets with a smooth surface is to vulcanise them on the special Berstorff Vulcanising Machine. This machine has a certain number of heated and polished drums, round which the rubber sheet runs without being wrapped. The time for passing it through the machine can be regulated, so that when the rubber sheet reaches the other end of the machine, it is completely vulcanised—Berstorff says, in 2 minutes.

Another way to obtain sheets with smooth surfaces is to wrap them between well smoothed twill round a drum, as has been described in Chapter III, when



Wrapping Machine. Fig. XXVIII.

dealing with the fabrication of the Gofferdam Plates, and then have them vulcanised.

Manhole washers and flat rings with or without insertion are made up of strips cut from uncured sheets by hand with a special knife. The strips are then put together and vulcanised in talc in closed boxes.

The following are some formulas for producing rubber sheetings:

Smoked sheets	....	10^k 000
Sulphur	....	0^k 200
Zinc Oxide Special	....	0^k 800
Vulkazit F (or its equivalent)		0^k 080
Stearic Acid	....	0^k 100
French Chalk (talc)	....	5^k 000
Silicious Chalk	....	7^k 500
Paraffin Wax	....	0^k 100
Aldolal Powder	....	0^k 100

N. B. The Aldolalphanaphthylamine Powder is added on the roller as soon as the rubber is masticated and before any of the fillers are incorporated.

The fabric for insertion is coated with the above mix, to which 1 kilo of Mineral Oil has been added. The mix is of a pale colour.

Vulcanisation: 20 minutes at 143° C.

Coloured Mixes can be obtained by adding to the above formula, the following:

Grey Mix: 20 to 40 grams Carbon Black.

Red Mix: 0^k 400 Red Iron Oxide.

Black Mix: 0^k 450 Carbon Black.

A cheaper quality of Packing sheeting is obtained from the following mix:

Smoked Sheets	....	10^k 000
Reclaim	....	30^k 000

Paraffin Wax	0^{k} 300
Stearic Acid	0^{k} 150
Zinc Oxide Special	0^{k} 800
Mineral Oil	1^{k} 000
Sulphur from	0^{k} 500 to 0^{k} 600
Vulkazit F	0^{k} 120
Silicious Chalk	26^{k} 000
Rosin Oil ...	0^{k} 300
Carbon Black (if required)	-

Cure: either 15 minutes at 151° C. or 25 minutes at 143° C.

This mix can be hardened by adding from 3 to 5 kilos of Kaolin, which will reduce cost price.

The following is a formula for sheetings of a superior quality used as carpets and the like:

White M2.

Pale Crepe	10^{k} 000
Flectol H	0^{k} 150
Zinc Oxide	5^{k} 000
Lithopone	5^{k} 000
Paraffin Wax	0^{k} 200
Cycline Oil	0^{k} 400
Stearic Acid	0^{k} 200
Silicious Chalk	22^{k} 500
Sulphur	0^{k} 300
Ureka White	0^{k} 150

Blue (for whiting purposes) a few grams.

Coloured M2 can be obtained by the addition of dyestuff.

The sheet wrapped on the drum is cured as stated hereafter.

With this formula, it is difficult to obtain the M2 perfectly white. This is due to the presence of anti-oxidant in the compound. As all anti-oxidants have a tendency to discolour, if the compound is to be exposed to sunlight, it would be better to do without an anti-oxidant, the ageing properties of the mix being assured by the addition of Ureka White.

If an Anti-oxidant is absolutely necessary, then the proportion of Flectol H should be reduced to from 1.5 to 0.20% on the weight of the raw rubber in the mix.

Another method of producing a pure white M2 mix is to increase the quantity of zinc oxide in the compound and to reduce proportionately the quantity of silicious chalk. Now if 20% of Titanium is added in the mix, the desired white shade will be obtained just after vulcanisation, but unfortunately, only for a short period, as Titanium or lithopone tends to darken the product after a few months, whereas with Zinc Oxide, the shade, although slightly cream, will be maintained for ever.

Let us now turn to the vulcanisation of M2. After trials, a cure of 45 minutes at 293° F. has been found to be satisfactory for a sheet of ¼" thickness, whereas for a sheet of ⅛" thickness, a cure of 15 minutes at 293° F. is the proper vulcanisation time. This can be further reduced say to 5 minutes provided the cure is effected at 307° F.

It is possible to reduce the time of cure of the M2 by reducing its Ureka content from 1.5% to 1.3% and by adding 0.2% of Thiuram on the weight of the raw rubber, with the result that a sheet of M2 of ⅛" thickness can be vulcanised in 5 minutes at 293° F., instead of in 15 minutes at the same temperature.

The addition of Thiuram, however, makes the compound scorchy, and one may anticipate a lot of troubles in the course of processing on the Mixing Roller.

If that is so, then one naturally wonders what kind of accelerated compound Berstorff is dreaming of when he states that with his vulcanising machine a rubber sheet can be vulcanised in 2 minutes, i. e. the time required for the sheet to pass through it. Then, if after all his vulcanising machine is really dependable, its speed should be reduced so that the sheet may pass through it, say in 5 minutes instead of 2, the former being already a very reasonable time for vulcanising rubber, but the drawback of the vulcanising machine is that the production of a few yards in five minutes is rather a restricted production.

The following is a pure white M2 mix, which is highly recommended:

Pale Crepe	10^{k} 000
Zinc Oxide Special	10^{k} 000
Lithopone	5^{k} 000
Paraffin Wax	0^{k} 200
Cycline Oil	0^{k} 400
Stearic Acid	0^{k} 200
Silicious Chalk	17^{k} 500
Sulphur	0^{k} 300
Ureka White	0^{k} 130
Thiuram	0^{k} 020
Ultra Zinc DMC (instead of Flectol H)	0^{k} 015

Cure: 5 minutes at 293° F. for a sheet of $\frac{1}{8}''$ thickness.

Mix for *Acid proof Sheeting:*

Crepe	10^{k} 000
Barytes or Silicious Chalk	22^{k} 500
Zinc Oxide	0^{k} 500
Sulphur	0^{k} 275
Mineral Rubber	2^{k} 000
Ureka	0^{k} 100
Paraffin Wax	0^{k} 200

Cure in open steam: 25 minutes at 141° C. or 287° F.

A *Black Mix* for the same purpose can be obtained by reducing the Baryte or Silicious Chalk and replacing it by 20 to 30 parts of Carbon Black.

It is to be noted that the addition of Paraffin Wax will give the mix a *blooming effect.* So for packing sheets it is advisable to avoid the paraffin wax, as the blooming effect renders the adherance of the rubber sheet very difficult.

The following is a Mix for acid proof *Hospital Sheetings* to be drawn on the Calender in 1 mm. thickness:

Crepe	10^{k} 000
Zinc Oxide	0^{k} 500
Lithopone	2^{k} 500
Kaolin	3^{k} 000
Baryte or Silicious Chalk	7^{k} 500
Sulphur	0^{k} 225
Ureka White	0^{k} 160
Paraffin Wax	0^{k} 200

For *Black Hospital Sheetings* (acid proof), instead of Lithopone, add a small quantity of Carbon Black, just to colour the compound.

For *Coloured Hospital Sheetings* (acid proof), the above formula, including Lithopone, may be employed with the addition of a few grams of the dye required.

All the above Hospital Sheetings can be wrapped on the drum in a fine fabric, which, after vulcanisation, will give to the surface of the sheet a fine impression of the fabric.

If a smooth surface is required, the sheet should be wrapped, as already explained, in a fine twill well rubberised, previously vulcanised, and coated with Shellac.

For this kind of smooth-surfaced sheetings, the vulcanisation should be done in hot air, rising for 90 minutes at 250° F. and keeping at that temperature for a further period of 50 minutes.

Electric-current-resisting Sheetings for use in Power Houses capable of resisting from 12,000 to 15,000 K. V. A. can be made from the following compound:

Crepe	....	5^{k} 000
Zinc Oxide	....	0^{k} 500
Sulphur	....	0^{k} 125
Paraffin Wax	....	0^{k} 060
Mineral Oil	....	0^{k} 100 (Cycline Oil)
Stearic Acid	....	0^{k} 025
Ureka	....	0^{k} 060

Cure in press for sheetings of 1″ thick, 25 minutes at 151° C. or 304° F.

Sheetings for Rubber Washers for Hydraulic Pumps are made from the following mix:

Smoked Sheets	....	10^{k} 000
Carbon Black Arrow		2^{k} 500
Kaolin	....	2^{k} 000
Tackol	....	0^{k} 300
Zinc Oxide	....	0^{k} 500
Ureka White F	....	0^{k} 125
Stearic Acid	....	0^{k} 200
Sulphur	....	0^{k} 300

Cure: wrapped in fabric, 30 minutes at 142° C.

X-Ray Proof Sheetings are obtained from the following mix:

Smoked Sheets	....	9^{k} 000
Sulphur	....	1^{k} 250
Litharge	....	120^{k} 000

Cure to be effected at 138° C. or 280° F. The duration of the cure depends upon the thickness of the sheeting. Litharge having a strong activating effect, neither accelerator nor zinc oxide is necessary in the above compound. The proportion of Sulphur is to be very high, as Litharge reacts with sulphur during vulcanisation, producing a sulphite of lead. If a lesser quantity of sulphur is used in the compound, the cure will be unsatisfactory.

Mixes for Rubber Stamp Sheetings:

A.	Smoked Sheets	10^{k} 000
	Zinc Oxide Special	1^{k} 000
	Baryte or Silicious Chalk	7^{k} 500
	Whiting	0^{k} 500
	Sulphur	0^{k} 450
	Vulkazit F	0^{k} 035
	Stearic Acid	0^{k} 080
	Paraffin Wax	0^{k} 080
	Aldolal Powder	0^{k} 030
	Mineral Oil	0^{k} 300
	Litharge	0^{k} 400

Cure: 6 to 8 minutes at 151° C. or 304° F.

Litharge is now rarely used in compounds of this class, because, apart from it being a poison, it has a tendency to scorch the mix and render the milling process very difficult. In addition a mix with litharge has a short life.

For these reasons, the following mix is recommended:

B.	Smoked Sheets	10^{k} 000
	Zinc Oxide Special	1^{k} 000
	Barytes or Silicious Chalk	7^{k} 500
	Whiting	5^{k} 000
	Sulphur	from 0^{k} 450 to 0^{k} 500
	Vulkazit F	0^{k} 450
	Stearic Acid	0^{k} 050
	Paraffin Wax	0^{k} 080

Aldolal Powder	0^{k} 030
Mineral Oil	0^{k} 300 to 0^{k} 500
Carbon Black (as a dye)	0^{k} 020

Cure: 6 to 8 minutes at 155° C. or 312° F.

Below are some *cheap Sheeting Mixes:*

A.	Scrap Rubber	2^{k} 500
	Zinc Oxide	0^{k} 125
	Lithopone	0^{k} 125
	Sulphate of Barium	3^{k} 500
	Stearic Acid	0^{k} 050
	Whiting	6^{k} 250
	Sulphur	0^{k} 075
	Ureka	0^{k} 037½
	Cycline Oil	0^{k} 250
	Paraffin Wax	0^{k} 100

Cure: 25 minutes at 151° C. or 304° F.

B.	Scrap Rubber	2^{k} 500
	Carbon Black P 33	0^{k} 500
	Zinc Oxide	1^{k} 500
	Carbon Black Arrow	0^{k} 125
	Sulphate of Barium	1^{k} 000
	Aldolal Powder	0^{k} 037½
	Flectol H	0^{k} 025
	Stearic Acid	0^{k} 025
	Sulphur	0^{k} 030
	Ureka	0^{k} 037½
	Paraffin Wax	0^{k} 037½
	Reclaimed Rubber	1^{k} 000

Cure: 25 minutes at 151° C. or 304° F.

Asbestos Sheetings for high steam pressure are manufactured by the following process on a special mixing roller.

The composition of the mix is about 80 to 85% of long fibre asbestos to be added to a solution of 2 parts of rubber to one part of litharge dissolved as a fairly thin solution in naphtha.

A special mill is used for this purpose with one roll of the normal mill roll size and another having a diameter of about 5ft. and running at a ratio of about 2 to 1. Both rolls are steam heated, and kept very hot. The mill has a special control which allows the nip to be widened slowly.

The asbestos-rubber-solution-mixture is thrown on to the nip when it is practically tight. This allows a thin film of the composition to be built upon the larger roll. When this is done, the adjustment is regulated so that the nip gradually opens, allowing the film on the large roll to increase in thickness.

This procedure is continued until the desired thickness is built up, and the sheet is then cut from the large roll.

No vulcanisation is given to this stock, as, when the compound, which is largely asbestos combined with a little rubber, is in service, sufficient vulcanisation takes place owing to the temperature condition existing at the joints.

Printed Rubber Sheets: Calendered sheets from the following compound:

Crepe	5^{k} 000
White Factice	4^{k} 000
Titanium White	0^{k} 400
Carbonate of Magnesium	0^{k} 200
Anti-oxidant RR5	0^{k} 100

are printed—before or after vulcanisation—with a printing paste compound consisting of about:

Crepe	10^{k} 000
Vulcan dyestuff	3^{k} 000
Titanium White	1^{k} 100

IG Unbleached Wax B	0^{k} 400
White Factice ...	4^{k} 000

The above mix, after being prepared on the mixing roller, is dissolved in an equivalent quantity by weight of benzine. The resulting paste, which is very viscous, is generally used for printing with a double tone printing steel roller. The printing dyes used are of fast vulcan colours.

The curing of the sheet is done with sulphur chloride either for about 20 minutes in the sulphur chloride vapour at 105° F. or for 5 to 10 seconds dipped in a 2% sulphur chloride benzine solution.

The drawn blue edge is made by kelting a thin blue sheet, on a special machine, and pasting it on the printed sheet by means of a rubber solution.

The pleating of the blue rubber can also be done by running the unvulcanised stock through an ordinary sewing machine with a pleater attachment.

Another mix for making these rubber sheets is as follows:—

Crepe	10^{k} 000
White Factice	3^{k} 000
Silicious Chalk	7^{k} 000
Sulphate of Barium	6^{k} 000
Ozokerite	0^{k} 050
Carbonate of Magnesia	0^{k} 300
Dyestuff	-

The sheet is generally of 0.25 mm. thickness and is cured with Sulphur Chloride as stated above.

For a white stock, 0^{k} 800 to 1^{k} 600 of lithopone should be added to the mix.

Coloured mixes are produced by using Vulcan Fast dyestuffs with the addition of from 0^{k} 200 to 0^{k} 400 of Titanium Dioxide.

To ensure resistance to ageing, it is absolutely necessary to add to the mix Carbonate of Magnesia.

For a smooth surface, a larger quantity of white factice is required when drawing the sheets on the calender.

The sheets, immediately after they have been drawn, are powdered with maize, polished and then printed. The printing is done on a machine very similar in construction to that used for the printing of textile goods. It may be done simultaneously with several colours. The printing rollers, however, should not be made of alloys containing copper as this will tend to destroy the rubber after some time.

After printing, the sheets with their blue edges are cut and shaped by special small machines supplied by Berstorff and others.

After shaping, the sheets are cured in a wooden drum by the following method. About 40 to 70 grams of Sulphur Chloride per cubic meter of the contents of the drum is evaporated into a case of proportionate dimensions, in which the drum rotates slowly. The vapour thus produced is to enter the drum through microscopic slits or holes, with which the sides of the drum are provided, and vulcanisation takes place in about thirty minutes. When the cure is completed, air is sucked into the case for 15 minutes.

The dyestuff solution is made as already explained.

Instead of vulcanising the printed rubber sheet with sulphur chloride, Berstorff suggests that it can be vulcanised in his vulcanising machine. In this case the mix should include sulphur and an accelerator. But the question then arises as to the kind of accelerator to be used, which could accommodate itself with White Factice, an ingredient of absolute necessity in such compounds.

Marbled Sheets, also called mottled sheets, for carpets, door and bath mats, and for different moulded goods, are now highly appreciated by the general public. The manufacture of these sheets is not very difficult, provided the factory adopts a standardised fabrication:

1. The formula of mixes once established should be strictly adhered to;
2. the strips must always be of the same size and length;
3. the rolls of the mixing Rollers and Calender must be widened always at the same opening and heated always at the same temperature.

When these principles are strictly observed, there cannot be any difficulty in the manufacture of Marbled Sheets.

The mix which we advise for this fabrication is the *M2 White* and *M2 coloured*, which formulas are given in this chapter. Two mixing rollers are used for this fabrication, one for each colour, say white and black. The rollers of the Mixing machine, as also the rollers of the Calender, should be kept 3 mm. apart. When the mixes are softened, strips of not more than 5 cm. in width and of length just enough to allow the two ends to join round the mixing roll are cut from them. A white strip and a black strip are twisted together. This should be done as quickly as possible, so that the strips may not cool down much. The twisted strips are then laid on the roller, their ends first. When all the strips have been so placed, the mixing roller is put in motion, and so a sheet is formed round the cylinder spotted white and black (see fig. XXIX). The sheet is then cut from the Mixing Machine and rolled by hand. This roll is introduced into the calender lengthwise and is delivered on the other side

Fig. XXIX.

coming out as a marbled sheet. If the design so obtained is not what one desires, the sheet is once again rolled by hand and introduced lengthwise through the calender for the second time. From the calender, the marbled sheets are supplied to the Moulding Section for further processes, or if the sheets are to be supplied as they come from the calender, they are wrapped on the Wrapping Machine between fine canvas, then vulcanised and the edges trimmed off, the marbled sheets thus being ready for despatch.

Another method of making marbled sheets is as follows:

The white mix M2 is run on the Mixing Roller and small strips of black M2 are thrown on the roller while it is in motion. The white and black compounds are allowed to mix together only partially. Care should be taken that both the colours are not completely mixed up, as there would then be no marbled sheet at all.

The mix is then cut from the mixing roll and passed through the calender, where a fine marbled sheet appears. In our opinion, this method is to be preferred to the one first described, as the finished sheet has a better appearance and the marbled designs look nicer.

Door and Bath Mats are cut to the required size from the vulcanised marbled sheet and punched to produce any attractive designs.

Marbled Moulded Goods, such as soap dishes, curtain cord tassels and shock proof electrical lampstands are produced from the following mix:

Pale Crepe	....	10^k 000
Silicious Chalk	....	17^k 500
Kaolin	....	5^k 000
Mineral Oil	....	0^k 250

Zinc Oxide	0^{k} 500
Sulphur	0^{k} 280
Stearic Acid	0^{k} 120
Vulkazit F	0^{k} 120
Ozokerite	0^{k} 100
Vulcan colour	-

Cure: 10 minutes at 151° C. or 304° F.

The following is a formula for *Hard Floor Tiles* stock of a shore hardness of about 94%.

Pale Crepe	10^{k} 000
Zinc Oxide	5^{k} 000
Lithopone	4^{k} 000
Sulphur	0^{k} 380
Vulkazit F	0^{k} 160
Stearic Acid	0^{k} 100
Paraffin Wax	0^{k} 120
Silicious Chalk	30^{k} 000
Whiting	10^{k} 000
Beewax	0^{k} 750
Mineral Oil	0^{k} 250
Vulcan colour	-

Cure in the Press: 15 minutes at 151° C. or 304° F.

A stock with a shore hardness of about 73% can be produced according to the following formula:

Pale Crepe	10^{k} 000
Silicious Chalk	20^{k} 000
Zinc Oxide	0^{k} 800
Lithopone	0^{k} 200
Sulphur	0^{k} 250
Vulkazit F	0^{k} 070
Vulkazit Thiuram	0^{k} 010
Stearic Acid	0^{k} 080
Ozokerite	0^{k} 100
Vulcan colour	-

Cure in the Press: 10 minutes at 143° C. or 289° F.

Another stock for *Marbled Flame-Proof Tiles:*

Pale Crepe	10^{k} 000
Arubren	10^{k} 000
Silicious Chalk	22^{k} 500
Mineral Oil	0^{k} 250
Zinc Oxide	0^{k} 500
Sulphur	0^{k} 280
Stearic Acid	0^{k} 120
Vulkazit F	0^{k} 120
Ozokerite	0^{k} 100

Cure in the Press: 10 minutes at 151° C. or 304° F.

When these tiles are moulded in bronze-tinned moulds, they will have a glazed surface after removal from the moulds.

The following is a formula for *Marbled hard Rubber for lamp stands:*

Pale Crepe	10^{k} 000
Sulphur	3^{k} 800
Silicious Chalk	5^{k} 000
Linseed Oil	0^{k} 200
Vulkazit DM	0^{k} 200
Carbonate of Magnesia	0^{k} 200
Vulcan dyes	-

The weight of the dyestuffs should be calculated on the weight of the mix.

Cure: about 90 minutes at 151° C. or 304° F.

Special Glue for affixing Rubber Tiles to Cement or Wooden Floors (from the Imperial Chemical Industries).

This Glue is prepared by measuring equal parts of the glue powder and cold water. The powder should be added to the water, stirring steadily for about ten minutes, and then allowing the mixture to stand for *at least* 30 minutes before use.

The life of the mixture when prepared is about 6 hours, therefore only sufficient should be made up in the morning for one half day's work. By thoroughly mixing the contents of the drum, before use, a good consistant average adhesion is obtained. The Glue can be stored, however, in closed drums and it is recommended that the drums be reversed from time to time, say once a month or so, so that the compounds on the top may gradually filter through to the bottom. After placing the tiles the best result is obtained when the floor surface is lightly rolled with a medium weight garden roller, and after rolling, a certain amount of pressure should be applied to the top of the surface, for example sand bags applied across the surface and left for about 12 hours to permit thorough cohesion.

Other cements for affixing Rubber Tiles to cement or wooden Floors are as follows:—

Adhesives for the Rubber Flooring:

1.	Soft alkali regenerator	100^{k} 000
	Resin	100^{k} 000
	Fresh slaked lime	1^{k} 500

This solution is swelled to the desired brushing consistency with benzine or naphtha.

2.	Resin	50^{k} 000
	Mineral Oil, Pale, refined	50^{k} 000
	Manilla Copal	37^{k} 500
	Asbestine	38^{k} 000
	Venetian Turpentine	2^{k} 500
	Methylated Spirit	22^{k} 000
3.	Gutta Percha	1^{k} 000
	Linseed Oil	1^{k} 200
	Ground waste from tyre tubes &c.	2^{k} 000
	Asphalt Pitch	5^{k} 000
	Resin	6^{k} 000

These mixes are melted up at a temperature of about 250°. *Before use* the mix is boiled up and small surfaces are coated. This is chiefly applicable to tiles, small sheets, etc. *but not for long strips.*

4.	Raw Rubber	2^{k} 500
	Gutta Percha	10^{k} 000
	Resin	12^{k} 500

This is mixed on the roller mill, drawn to plates, and dissolved in the stirring mill with benzine, carbon tetrachloride, dichlorethylene, etc.

5.	Shellac	2^{k} 500
	Gypsum	7^{k} 500
	Methylated Spirit	1^{k} 800
	Carbon Tetrachloride	1^{k} 800

CHAPTER IX.

Press Cured Goods.

MANY articles in the rubber industry are press cured. For this purpose, rubber is generally prepared from calendered sheets, which are doubled to the required thickness and, the blisters having been carefully removed, cut to size and shape and then moulded.

Planed wrought-iron rings and frames aré used for producing circular and other valves, and when filled with rubber, the articles are cured under suitable pressure. Soles and heels are cured in engraved moulds. There are other articles which are made in moulds of a complicated construction. When calculating the capacity of the moulds, it must be remembered that the rubber to be vulcanised will contract slightly after cure. This is caused by the cooling down of the articles and the way in which the rubber was stretched previously. Higher grades of rubber contract from 2½% to 3% of the extent of their surface; lower qualities contract proportionately less. In the latter case the thickness decreases, whilst in the former it increases slightly. Special attention must be given to this fact when building the moulds.

We have seen in Chapter VIII of the First Part of this book, how to keep the moulds in perfect working condition, and it should be borne in mind that they must always be well cleaned, free from dirt and rust, and that mould paste should be administered to the inner part which comes into contact with the rubber. This will ensure the production of moulded goods of nice appearance.

In this chapter, we shall see what can be produced in the moulds.

Herewith we give a few formulas for moulded goods, which proved very satisfactory in practical factory work.

(A) Moulded Tyres for Electrical Trucks etc.

1. *Hard Rubber Base:*

Smoked sheets	10^{k} 000
Reclaim Rubber	5^{k} 000
Ebonite Dust	5^{k} 000
Whiting	7^{k} 500
Linseed Oil	0^{k} 300
Sulphur	6^{k} 000
Carbonate of Magnesia	1^{k} 000
Vulkazit CT	0^{k} 200

2. *Soft Rubber Covering:*

Smoked sheets	5^{k} 000
Crepe	5^{k} 000
Zinc Oxide	8^{k} 000
Carbon Active *Micronex*	0^{k} 500
Neutral Carbon P 33	2^{k} 500
Phenylbetanaphthylamine	0^{k} 120
Tackol	0^{k} 200
Sulphur	0^{k} 420
Vulkazit D	0^{k} 080
Vulkazit FP	0^{k} 020

Cure in the Press: 80 to 90 minutes at 143° C. or 289° F.

For obtaining a harder stock, use Oil Soot Elastic instead of Carbon Black P 33.

(B) Mixes for Hard Soles:

1. *Brown:*

Smoked Sheets	10^{k} 000
Carbonate of Magnesia	16^{k} 500
Light Magnesia	1^{k} 500
Zinc Oxide Special	1^{k} 000
Montan Wax	0^{k} 500
Red Iron Oxide 720	0^{k} 500
Phenylbetanaphthylamine	0^{k} 100
Mineral Rubber	4^{k} 000
Silicious Chalk	4^{k} 000
Sulphur	0^{k} 400
Vulkazit F	0^{k} 200
Stearic Acid	0^{k} 200

Cure in the Press: 10 to 15 minutes at 151° C. or 304° F.

2. *Black.*

Smoked sheets	10^{k} 000
Carbon Black Arrow	12^{k} 000
Zinc Oxide Special	1^{k} 000
Mineral Rubber	4^{k} 000
Stearic Acid	0^{k} 400
Silicious Chalk	1^{k} 500
Sulphur	0^{k} 400
Vulkazit F.	0^{k} 200
Phenylbetanaphthylamine	0^{k} 100

Press Cure: 10 to 15 minutes at 151° C. or 304° F.

3. *Soles with low specific gravity:*

Crepe	10^{k} 000
Sulphur	0^{k} 285
Acid Stearic	0^{k} 150
Vulkazit F	0^{k} 080

Vulkazit Thiuram	0^{k} 110
Lithopone	0^{k} 100
Silicious Chalk	1^{k} 500
Zinc Oxide Special	0^{k} 500

Cure in the Press: 20 minutes at 143° C. or 289° F.

4. *Brown Heel Stock:*

Smoked sheets	10^{k} 000
Mineral Rubber	1^{k} 200
Magnesium Carbonate	8^{k} 600
Red Iron Oxide 720	0^{k} 350
Sulphur	0^{k} 300
Zinc Oxide Special	1^{k} 100
Vulkazit F	0^{k} 125
Magnesium Oxide heavy	1^{k} 500

Cure in the Press: 10 to 12 minutes at 151° C. or 304° F.

5. *Cheap Brown Heel Stock:*

Smoked sheets	10^{k} 000
Reclaim from tyres	12^{k} 000
Red Iron Oxide 720	0^{k} 500
Mineral Rubber	0^{k} 500
Zinc Oxide Special	2^{k} 000
Sulphur	0^{k} 550
Vulkazit F	0^{k} 200
Stearic Acid	0^{k} 150
Magnesium Carbonate	4^{k} 000
Silicious Chalk	25^{k} 000
Aldolal Powder	0^{k} 100

Cure in the Press: 12 minutes at 151° C. or 304° F.

6. *Cheap Heel Mix with Reclaim:*

Reclaim	10^{k} 000
Sulphur	0^{k} 320
Altax	0^{k} 120

Zinc Oxide	1^k 000
Rubberine-Gel	0^k 600
Carbon Black Arrow	2^k 600
Ground Waste in Powder without canvas	6^k 400

Cure in Press: 8 minutes at 153° C. or 307° F.

7. *Cheap Brown Mix for Soles and Heels:*

Scrap Rubber	2^k 500
Silicious Chalk	4^k 000
Zinc Oxide	0^k 250
Red Iron Oxide	0^k 100
Sulphur	0^k 075
Ureka	0^k 032
Flectol H	0^k 025
Tackol	0^k 100
Carbon black	0^k 008

Cure in Press: 25 minutes at 150° C. or 302° F.

8. *Cheap Black Mix for Soles and Heels:*

Scrap Rubber	2^k 500
Silicious Chalk	4^k 000
Zinc Oxide	0^k 250
Carbon Black Arrow	0^k 200
Sulphur	0^k 075
Ureka	0^k 032
Flectol H	0^k 025
Tackol	0^k 100

Cure in the Press: 25 minutes at 150° C. or 302° F.

9. *Brown Sole and Heel Mix:*

Smoked sheets	5^k 000
Silicious Chalk	3^k 750
Zinc Oxide	0^k 500
Sulphur	0^k 150
Red Iron Oxide 720	0^k 200

Tackol	0^{k} 300
Stearic Acid	0^{k} 100
Ureka	0^{k} 064
Flectol H	0^{k} 050
Carbon Black Arrow	0^{k} 008

Cure in the Press: 25 minutes at 150° C. or 302° F.

10. *Black Sole and Heel Mix:*

Smoked Sheets	5^{k} 000
Zinc Oxide	0^{k} 500
Carbon Black Arrow	0^{k} 500
Silicious Chalk	3^{k} 750
Tackol	0^{k} 300
Stearic Acid	0^{k} 100
Sulphur	0^{k} 150
Ureka	0^{k} 064
Flectol H	0^{k} 050

Cure in the Press: 25 minutes at 150° C. or 302° F.

11. *Soft Black Sole & Heel Mix*:

Smoked Sheets	2^{k} 500
Zinc Oxide	0^{k} 250
Carbon Black Arrow	0^{k} 250
Kaolin	1^{k} 875
Tackol	0^{k} 150
Stearic Acid	0^{k} 050
Sulphur	0^{k} 075
Ureka	0^{k} 032
Flectol H	0^{k} 025

Cure in the Press: 25 minutes at 150° C. or 302° F.

12. *Hard Black Soles and Heels:*

Smoked Sheets	2^{k} 500
Zinc Oxide	0^{k} 250
Carbon Black Arrow	0^{k} 500
Kaolin	4^{k} 000

Tackol	0^{k} 150
Stearic Acid	0^{k} 050
Sulphur	0^{k} 075
Ureka	0^{k} 032
Flectol H	0^{k} 025

Cure in the Press: 25 minutes at 150° C. or 302° F.

13. *Brown Soft Mix for Soles and Heels:*

Smoked Sheets	2^{k} 500
Zinc Oxide	0^{k} 250
Red Iron Oxide	0^{k} 250
Kaolin	1^{k} 875
Sulphur	0^{k} 075
Ureka	0^{k} 032
Flectol H	0^{k} 025
Tackol	0^{k} 150
Stearic Acid	0^{k} 050
Carbon Black P33	0^{k} 005

Cure in the Press: 25 minutes at 150° C. or 302° F.

14. *Brown Chappal Mix:*

Scrap	7^{k} 500
Kaolin	15^{k} 000
Zinc Oxide	0^{k} 300
Red Iron Oxide 720	0^{k} 150
Sulphur	0^{k} 225
Ureka	0^{k} 090
Mineral Rubber	0^{k} 150
Tackol	0^{k} 150
Flectol H	0^{k} 090

Cure in the Press: 25 minutes at 150° C. or 302° F.

15. *Black Chappal Mix*:

Scrap	2^{k} 500
Kaolin	4^{k} 500
Carbon Black Arrow	0^{k} 200

Sulphur	0^{k} 075
Ureka	0^{k} 030
Zinc Oxide	0^{k} 075
Tackol	0^{k} 150

Cure in the Press: 25 minutes at 150° C. or 302° F.

(C) **Rubber Button Mix:**

Crepe	2^{k} 500
Kaolin	5^{k} 000
Zinc Oxide	0^{k} 125
Paraffin Wax	0^{k} 040
Mineral Rubber	0^{k} 012
Sulphur	0^{k} 150
Ureka	0^{k} 035

Cure in the Press: 25 minutes at 150° C. or 302° F.

(D) **Rice Polishers:**

1. The Black upper part of the polisher is made of the following mix:

Smoked Sheets	2^{k} 500
Zinc Oxide	0^{k} 250
Carbon Black Arrow	1^{k} 000
Kaolin	0^{k} 500
Sulphur	0^{k} 070
Tackol	0^{k} 050
Flectol H	0^{k} 025
Stearic Acid	0^{k} 062
Ureka	0^{k} 030

2. The white part of the polisher is made of the following mix:

Crepe	5^{k} 000
Zinc Oxide	0^{k} 500
Pumice Powder	0^{k} 800
Kaolin	2^{k} 250
Sulphur	0^{k} 150

Ureka	....	0k 060
Paraffin Wax	....	0k 060
Stearic Acid	....	0k 025
Cycline Oil	....	0k 100

Cure in the Press: 25 minutes at 150° C. or 302° F.

The white surface is to be made rough by rasping with a file.

Mix recommended for Garry and Rickshaw Tyres:

Smoked Sheets	....	10k 000
Zinc Oxide	....	1k 000
Carbon Black Arrow		2k 000
Stearic Acid	....	0k 200
Tackol	....	0k 600
Silicious Chalk	....	7k 500
Sulphur	....	0k 350
Ureka	...	0k 110
Flectol H	....	0k 150

Special precaution is to be taken with this compound.

When the mix is ready on the Mixing Roller, it is allowed to rest for *eight days*, after having been cooled in water. Then it is extruded on the Forcing Machine, the mouth piece of which is heated to give a smooth surface, and cured in mould in the press.

Cure: for tyres 1¼″ thick 40 minutes at 290° F.
for tyres 1″ thick and less 25 minutes at 300° F.

These tyres can be cured also in talc, in open steam or rolled round a drum, in which case the time of vulcanisation is 60 minutes at 286° F.

Rubber Tyres for Bullock Cart Wheels. These are made by covering the iron band of the wheel with about one-sixteenth inch of ebonite. Then about one-quarter of an inch of a fairly heavily compounded tread must be laid on. Finally, for the remaining two-thirds a normal tread stock containing not less then 45% of Carbon Black must be built up. It will be necessary to use a relatively fast curing ebonite, since the cure of the whole tyre is to be completed in about 75 to 90 minutes at 138° C. or 281° F.

The following three mixes are recommended:

(a) **Ebonite Stock:**

Smoked Sheets	10^{k} 000
Sulphur	5^{k} 000
Dust Ebonite	8^{k} 000
Iron Oxide	1^{k} 000
Zinc Oxide	0^{k} 500
Thiotax	0^{k} 200
Ultra Zinc DMC	0^{k} 200

(b) **Intermediate Stock:**

Smoked Sheets	10^{k} 000
Zinc Oxide	1^{k} 000
Carbon Black Arrow	4^{k} 500
Lamp Black	4^{k} 000
Stearic Acid	0^{k} 200
Tackol	0^{k} 300
Sulphur	0^{k} 300
Ureka	0^{k} 125
Flectol H	0^{k} 100

(c) **Tread Stock:**

Smoked Sheets	10^{k} 000
Zinc Oxide	1^{k} 000
Carbon Black	4^{k} 500
Stearic Acid	0^{k} 200
Tackol	0^{k} 300
Sulphur	0^{k} 300
Ureka	0^{k} 125
Flectol H	0^{k} 100

The following are comments on the above formulas:

The (a) stock cures up to a good ebonite hardness in roughly 60 minutes at 134° C. or 274° F., which will approximate to the cure it will have if the whole tyre cures at 75 to 90 minutes at 138° C. or 281° F. If the ebonite is to cure slowly, the ultra Zinc DMC concentration should be increased from 2 to 3%. On the other hand, one may find that it can be dropped to 1½% or something less. Unfortunately, the accelerator cost of this stock is relatively high on account of the use of the Ultra Zinc DMC. But the latter cannot be dispensed with, if satisfactory cure in a reasonable length of time is to be obtained. Since so little of the stock is used, however, the cost should not be prohibitive.

The (b) formula is designed to give a stock of intermediate hardness in order to get satisfactory adhesion with the more flexible tread rubber and the hard ebonite layer. One may even find it desirable to increase the lamp black content still further.

Finally, the (c) formula is a straightforward tread stock for the outside, since it has to bear the weight of the bullock-cart and stand against the conditions of the road.

The only difficulty which may be experienced is that a little over-curing may take place at the point where the ebonite stock unites with the intermediate layer. This may have been brought about by the Ultra-Accelerator DMC and can be avoided by interposing a very thin layer of the (b) formula, *but without sulphur and accelerator.* The bullock cart wheel so coated with rubber is then tied between two paper covered flanges of the outer diameter of the wheel and is wrapped with strong canvas layers, so that the iron flanges fit tightly against the rubber. The wheel is then vulcanised in open steam at the above indicated cure. When this is done, the wheel is unwrapped, the iron bands removed and the rubber trimmed off, if there is overflow, and cleaned, the wheel then being ready for despatch.

Rubber Beltings. Cotton fabric of strong texture is frictioned on the calender so that a sticky layer of rubber is pressed upon it. Then the rubberised fabric is folded into belts of the desired width and the number of plies required. This is done either by a special machine or by hand. The excess fabric is cut away, or, if the material is a little too narrow, another piece is attached. After the insertions have been folded, the belt is run through the belting calender in order to be pressed and straightened out. A covering sheet of rubber may be put on according to the finish required, but this, however, is not necessary with well spread cotton fabric.

Beltings are cured either with angular edges in moulds, or with rounded edges, free under the hydraulic press, the latter being decidedly preferable. In order to prevent the beltings from stretching, when in use, they are, stretched under a press, provided with a special stretching device whilst being cured. To obtain a very strong article, the vulcanising press must work at a pressure of at least 40 kilos per sq. cm. and care must be taken that the temperature of fabrication is not raised above 275° F., as that would weaken the fiber of the fabric.

Beltings are also made *endless* without any difficulty, the fabric being so folded that the belting, when finished and well stretched, has the required circumference.

The following is a very good belting mix:

Smoked sheets	....	8^k 000
Crepe	....	2^k 000
Zinc Oxide	....	2^k 000
Phenylbetanaphthylamine		0^k 130

Tackol	....	0^k 200
Sulphur	....	0^k 100
Stearic Acid	....	0^k 080
Vulkazit F	....	0^k 130

Cure in the Press: 20 to 25 minutes at 132.8° C.

The following is a mix for moulded *Buffers, Springs, Brakes etc.*

Smoked Sheets	....	10^k 000
Sulphur	....	0^k 700
Rubberine-Gel	....	0^k 700
Mineral Rubber	....	0^k 200
Zinc Oxide	....	17^k 000
Litharge	....	1^k 400

Cure in the Press: 25 minutes at 292° F.

Eraser Rubbers. The suitably composed mixes are calendered into sheets and then doubled to the required thickness. They are then cut to say 500 x 500 mm. size and cured under the press in forged iron frames of the desired thickness.

After vulcanisation, the erasers are cut to size and allowed to remain for about 24 hours, preferably in a wooden hexagonal drum revolving slowly, and partially filled with pumice powder. During this time the erasers get polished and their edges smoothed. Erasers to be shaped must first be ground on the emery stone and then polished in the drum as stated above.

For *Union Rubber Erasers* for ink and pencil, the sheet after being pressed smooth in a cold press is cut into strips of the required width, care being taken that a clean cut is obtained. The cut edges are well brushed with a suitable vulcanising solution, and when dry are stuck together and subjected to a preliminary pressure and then vulcanised in frames under the press. They are afterwards cut to the required size and polished in the grinding drum.

The following are mixes for erasers of first quality:

(A) **For Ink and Typewriter Erasers:**

1.	Pale Crepe	10^{k} 000
	Zinc Oxide	1^{k} 000
	Titanium White	0^{k} 800
	Pumice Powder	6^{k} 000
	Silicious Chalk	10^{k} 000
	Ground Glass	10^{k} 000
	Setaric Acid	0^{k} 100
	Sulphur	0^{k} 250
	Paraffin Oil	1^{k} 000
	Vulkazit F	0^{k} 100

For white erasers, add to the above mix

Titanium White	5^{k} 000

For blue erasers, add

Titanium White	1^{k} 200
Vulcan Fast Blue CGF	0^{k} 150

Cure in the Press: 15 to 18 minutes at 300° F.

(B) **For Pencil Erasers:**

2.	Pale Crepe	10^{k} 000
	White Factice F 18	20^{k} 000
	Paraffin Oil	12^{k} 000
	Sulphur	0^{k} 650
	Magnesia Heavy quality	3^{k} 000
	Vulkazit 1000	0^{k} 200
	Vulkazit TR	0^{k} 050
	Lithopone	2^{k} 000

Cure in the Press: 30 minutes at 300° F.

3.	Pale Crepe	10^{k} 000
	Factice White	25^{k} 000
	Zinc Oxide Special	0^{k} 500
	Sulphur	0^{k} 500
	Lithopone	19^{k} 000

	Paraffin Oil	8^{k} 000
	Vulkazit Mercapto	0^{k} 160
	Dibutylamine	0^{k} 050
	Vulkazit H	0^{k} 050

Cure in the Press: 30 minutes at 300° F.

4.	Pale Crepe	15^{k} 000
	Factice White	23^{k} 000
	Magnesia light quality	3^{k} 000
	Paraffin Oil	6^{k} 000
	Pumice Powder	22^{k} 500
	Lithopone	3^{k} 000
	Sulphur	0^{k} 575
	Vulkazit TR	0^{k} 150
	Vulkazit 1000	0^{k} 150
	Vulcan Red 3 BF	0^{k} 225

Cure in the Press: 20 to 25 minutes at 300° F.

5.	Pale Crepe	18^{k} 000
	Factice R Special	45^{k} 000
	Magnesia Light quality	3^{k} 600
	Paraffin Oil	6^{k} 000
	Ground Glass	15^{k} 000
	Lithopone	15^{k} 000
	Sulphur	0^{k} 860
	Vulkazit TR	0^{k} 180
	Vulkazit 1000	0^{k} 180
	Silicious Chalk	22^{k} 500
	Vulcan Red BF	0^{k} 250
	Vulcan Fast Orange CF	0^{k} 100

Cure in the Press: 20 to 25 minutes at 300° F.

6.	Pale Crepe	15^{k} 000
	Factice R Special	40^{k} 000
	Magnesia light quality	3^{k} 500
	Mineral Oil	7^{k} 500
	Pumice Powder	10^{k} 000

Ground Glass 80	5^{k} 000
Lithopone	10^{k} 000
Sulphur	0^{k} 800
Vulkazit TR	0^{k} 200
Vulkazit 1000	0^{k} 150
Vulcan Red LCF	0^{k} 400
Vulcan Fast Orange GF	0^{k} 200

Cure in the Press: 25 to 30 minutes at 300° F.

7. Pale Crepe	15^{k} 000	14^{k} 000	14^{k} 000
Factice R Special	40^{k} 000	32^{k} 000	32^{k} 000
Magnesia light quality	3^{k} 500	3^{k} 000	3^{k} 000
Mineral Oil	7^{k} 500	3^{k} 000	3^{k} 000
Pumice Powder	10^{k} 000	20^{k} 000	10^{k} 000
Ground Glass 100	10^{k} 000	-	-
Lithopone	10^{k} 000	10^{k} 000	10^{k} 000
Sulphur	0^{k} 800	0^{k} 800	0^{k} 800
Vulkazit TR	0^{k} 200	0^{k} 220	0^{k} 220
Vulkazit 1000	0^{k} 150	0^{k} 140	0^{k} 140
Vulcan Red LCF	0^{k} 300	0^{k} 300	0^{k} 300

Cure in the Press: 30 minutes at 300° F.

	Red	*White*
8. Pale Crepe	10^{k} 000	10^{k} 000
White Fatice F 18	27^{k} 000	27^{k} 000
Mineral Oil	4^{k} 000	4^{k} 000
Silicious Chalk	15^{k} 000	10^{k} 000
Pumice Powder	7^{k} 000	7^{k} 000
Ground Glass	5^{k} 000	5^{k} 000
Lithopone	2^{k} 000	20^{k} 000
Sulphur	0^{k} 580	0^{k} 580
Vulkazit TR	0^{k} 130	0^{k} 120
Vulkazit 1000	0^{k} 100	0^{k} 100
Vulcan Fast Orange	0^{k} 160	-
Vulcan Rubine BRF	0^{k} 060	-
Magnesium light quality	3^{k} 000	3^{k} 000
Stearic Acid	0^{k} 200	0^{k} 200

Cure in the Press: 35 to 40 minutes at 300° F.

It will be noted that either *White* or *Brown Factice* forms one of the ingredients in the above mixes notwithstanding the fact that it has been remarked elsewhere in this book that White and Brown Factices rarely accommodate themselves with most of the existing accelerators, which is likely to cause a lot of difficulties to Rubber Technologists who have to prepare mixes for erasers and for coating of printing rollers and the like, in which the presence of Factice is a necessity.

As may be seen, however, from the above formulas, Vulkazit 1000 and TR can be combined with fillers in mixes which contain White Factice. Monsanto affirm that in certain cases their Ureka White has proved very satisfactory when combined with White Factice, provided sufficient Carbonate of Magnesia is present in the stock to make good the effect of acidity caused by White Factice.

When composing mixes containing Factices, the Rubber Technologist will have to bear in mind that Brown Factice absorbs sulphur and that to prevent lack of sulphur produced thereby, he has to increase its quantity in the mix say by 4 to 4½% calculated on the combined weight of raw rubber and Brown Factice present in the stock.

In the case of White Factice, it produces a certain amount of free hydrochloric acid during vulcanisation, which kills the action of most of the existing accelerators. It is therefore very important to determine the approximate acidity of the White Factice used, so that a corresponding quantity, say 5 to 10% of Carbonate of Magnesium—MgO—may be added to the stock. The drawback, however, of Carbonate of Magnesia is that the presence of this filler in certain stocks makes them scorchy, particularly when mixes are drawn on the calender and when they contain organic accelerators.

The Factices we would recommend for use in rubber compounds must, on analysis, show the following properties:

	After incineration % ash	% of free sulphur	% of acetone extract
White Factice	3^{k} 5	0^{k} 6	4^{k} 0
Brown Factice	4^{k} 5	5^{k} 0	15^{k} 0

The specific gravity of White Factice should, on an average, be 1.000 and of Brown Factice 1.022.

CHAPTER X.

Ebonite.

EBONITE, also called *Hard Rubber*, is produced from rubber compounds in which the proportion of sulphur and accelerator, compared with that in soft compounds, is rather high. The method of preparing ebonite stock, on the Mixing Roller, is identical to that for ordinary mixes, and when coming out from the mixer, the ebonite stock is either calendered in sheets or extruded on the Forcing Machine. The vulcanisation of ebonite takes a longer time than that of soft rubber, and in fabrication this is the only difference between ebonite and soft rubber compounds.

When ebonite is vulcanised; it is very hard, and can be worked on the lathe with tools of special steel, and then polished, as will be explained later. Surgical and Sanitary accessories, and also several items for insulating purposes, are made from ebonite.

In the manufacture of solid tyres for lorries and bullock carts, it is the ebonite which is immediately in contact with the iron base, and it is on the ebonite that the tread stock is built.

Combs, penholders, fountain pens and the like can be made of ebonite. The rather complicated process of manufacturing ebonite penholders, is explained as follows:

The moulded ebonite compound is vulcanised first for a short time, so that after cure, the stock is still soft. Twelve penholders are moulded in one mould. When so vulcanised, they are not in the shape of a penholder. Then they are fully vulcanised separately in talc boxes and straightened, on plain iron plates when still warm, and consequently soft, as warmed ebonite is always soft. In the case of spiral shaped penholders, they are shaped against an emery stone, so that they are four-faced. Then they are warmed a second time, and the point being kept fixed, they are twisted by hand so that the penholder has now a spiral shape, which is dipped in cold water, thus allowing the spiral shape to remain. The other end of the penholder is then hollowed out, into which is fixed the ebonite bush to hold the nib.

Penholders thus prepared are put in a wooden drum, the inner side of which is shaped like a polygon. The drum is half filled with pumice stone powder and is put in motion for hours, if not days, till the penholders have a very smooth surface.

Then they are mounted on frames which move forwards and backwards under a roller fitted with round pieces of woollen cloth fitted on an iron axle running at a somewhat high speed. A few drops of linseed oil will be sprinkled on the penholders from time to time till they are perfectly polished. The article is then ready for packing.

It may be said that not less than two weeks are necessary to manufacture a penholder, but thousands can be made at a time.

Combs are made by the employment of a similar process, except that the teeth of the combs are produced on special cutting machines, the various discs of which are so arranged that one push would provide the comb with its teeth.

Battery Cases are either moulded, or made by hand, on galvanised forms having the inside shape of the battery case. Sheets of ebonite are cut to size, pasted together, and wrapped in wet fabric on which are placed galvanised sheets of the size of the battery case. The whole is then wrapped in wet fabric and vulcanised. They are removed from the galvanised forms and the outer surfaces are smoothed on a large emery stone and finished to shape, after which they are either dusted with mica powder, or simply cleaned with linseed oil, to be ready for packing.

The author has produced for years what may be called *Armoured Ebonite*—a combination of hard and soft rubber, separated by rubberised felt or any other rubberised fabric, the ebonite stock being either acid-proof or electric-proof, as the case may be. When only one layer of fabric is needed several holes are punched in it in such a manner that there may be an effective connection between the layers of ebonite and soft rubber composing the ebonite armoured sheet. In case the ebonite is to be armoured with two or more plies, the holes of these plies are punched in such a way that the position of the holes in one ply dose not correspond with the position of the holes in other ply. The sheet is made as follows: first an outer layer of ebonite, then a ply of soft rubber and upon it another ply of rubberised felt or fabric, and finally the last ebonite layer, the whole being vulcanised in the press in a frame, or in a mould. In our opinion for battery cases, armoured ebonite should always be used as with the ordinary ebonite case, a shock or blow may break the wall, with the result that the acid is lost and the battery case put out of service. With armoured ebonite, when a case is damaged, the outer surface may break, but the shock is absorbed by the soft rubber inside the sheet, kept together with the plies of felt or fabric, and the battery case remains in working condition.

The advantages of armoured ebonite, compared with ordinary ebonite, are: greater tensile strength, greater flexibility, greater resistance to breakage and improved durability.

Below are a few formulas for very good ebonite stocks:

Black Ebonite with Vulkazit F.

Smoked Sheets	10^{k} 000
Sulphur	6^{k} 500
Gas Soot	1^{k} 000
Vulkazit F	0^{k} 200
Ebonite Dust	6^{k} 000
Reclaim Rubber	5^{k} 000
Whiting	4^{k} 000

Cure: about 120 minutes at 147° C. or 297° F. according to thickness of the sheet.

Black Ebonite with Vulkazit CT:

Smoked Sheets	10^{k} 000
Sulphur	4^{k} 500
Linseed Oil	0^{k} 200
Vulkazit CT	0^{k} 150
Magnesia Carbonate (light)	0^{k} 300
Gas Soot	0^{k} 500

Cure: about 80 minutes at 147° C. or 297° F. according to the thickness of the sheet.

Mixes for Coloured Ebonite:

Red:	Smoked Sheets	10^{k} 000
	Sulphur	4^{k} 000
	Linseed Oil	0^{k} 200
	Vulkazit CT	0^{k} 150
	Light Carbonate of Magnesia	0^{k} 300
	Red Iron Oxide 720	3^{k} 000

Cure: 60 to 80 minutes at 147° C. or 297° F. according to the thickness of the sheet.

Red:	Pale Crepe	10^{k} 000
	Sulphur	4^{k} 000
	Linseed Oil	0^{k} 200
	Vulkazit F	0^{k} 200
	Vulcan Red LG	0^{k} 350
	Kaolin	6^{k} 000
	Vulcan Resine Red B	0^{k} 150
	Cadmium Red B	0^{k} 900

Cure: 120 minutes at 147° C. or 297° F. according to the thickness of the sheet.

Green:	Pale Crepe	10^{k} 000
	Sulphur	4^{k} 000
	Linseed Oil	0^{k} 200
	Vulkazit F	0^{k} 200
	Silicious Chalk	2^{k} 500
	Lithopone	0^{k} 500
	Vulcan Fast Blue GG	0^{k} 200
	Vulcan Fast Yellow 5G	0^{k} 600

Cure: 120 minutes at 147° C. or 297° F. according to the thickness of the sheet.

The above five mixes, when vulcanised at 151° C. or 304° F. will be porous, and it is therefore recommended to vulcanise them at a lower temperature for a longer period.

Ebonite Mix for Moulded Goods:

Smoked Sheets	10^{k} 000
Sulphur	4^{k} 000
Monsanto A 7	0^{k} 200
Ebonite Dust	20^{k} 000

Cure: about 3 hours at 286° F.

Black Ebonite Mix with Ureka:

Smoked Sheets	2^{k} 500
Zinc Oxide	0^{k} 125
Ureka	0^{k} 050

Stearic Acid	....	0^k 090
Pine Tar	....	0^k 063
Sulphur	....	1^k 125
Whiting	....	0^k 750
Black	....	1^k 000

Cure: 1 hr. 45 mins. at 304° F.

Red Ebonite Mix with Accelerator 201:

Pale Crepe	....	2^k 500
Zinc Oxide	....	0^k 125
Accelerator 201	....	0^k 050
Stearic Acid	....	0^k 090
Pine Tar	....	0^k 063
Sulphur	....	1^k 125
Whiting	....	0^k 750
Red Iron Oxide	....	1^k 000

Cure: 1 hr. 45 mins. at 304° F.

Acid-Proof Ebonite for Press Moulded Battery Cases:

Smoked Sheets	....	5^k 000
Zinc Oxide	...	0^k 250
Accelerator 201	....	0^k 100
Stearic Acid	....	0^k 180
Pine Tar	....	0^k 125
Sulphur	....	2^k 250
Sulphate of Barium	....	3^k 500
Ebonite Dust	....	2^k 000

Cure: in mould 25 minutes at 304° F., then in water or talc 1 hr. at 304° F.

Another Acid-proof Ebonite mix for Battery Cases:

Smoked Sheets	....	2^k 500
Sulphur	....	1^k 125
Heavy Carbonate of Magnesia		0^k 125
Ebonite Dust	....	1^k 000
Silicious Chalk	....	3^k 750
Mineral Rubber	....	2^k 000
Accelerator 201	....	0^k 050

Cure: 1 hr. 45 mins. at 304° F.

Following are 2 Ebonite Acid-Proof Mixes for Battery Cases:

A.	Smoked Sheets	10^{k} 000
	Alkali Reclaim	10^{k} 000
	Sulphur	7^{k} 600
	Carbonate of Magnesia (heavy)	1^{k} 000
	Ebonite Dust	6^{k} 000
	Sulphate of Barium	15^{k} 000
	Mineral Rubber	4^{k} 000
	Vulkazit CT	0^{k} 300
B.	Smoked Sheets	10^{k} 000
	Sulphur	4^{k} 500
	Carbonate of Magnesia (heavy)	0^{k} 500
	Ebonite Dust	4^{k} 000
	Silicious Chalk	15^{k} 000
	Mineral Rubber	8^{k} 000
	Vulkazit CT	0^{k} 200

Cure in the Press: for a sheet of 12 mm. thick, from 45 to 60 mins. at 300° F. (The exact cure should be fixed after trials on the spot under factory conditions).

If the cure is combined, pre-vulcanisation should be in the press and final vulcanisation in open steam.

In the Press: 8 to 12 minutes at 302° F.

In open Steam: for Mix A, about 55 mins. at 300° F.
for Mix B, about 65 mins. at 300° F.

There is a very simple and good *Ebonite Mix with DPG Accelerator*, as follows:

Smoked Sheets	10^{k} 000
Sulphur	5^{k} 000
Carbonate of Magnesia (heavy)	5^{k} 000
D. P. G.	0^{k} 300

Cure: 1 hr. at 148° C.

By adding to the above mix some more fillers and ebonite dust, the time of cure can be reduced proportionately.

Ebonite can be produced in a *white ivory shade* with the incorporation of Accelerators 201 and 501 and by using as pigments *Titanium White*, *Zinc Sulphite* and *Zinc Oxide*, to be vulcanised at low temperature, about 75 to 105 minutes at 304° F. for a sheet of 4 mm. thickness.

Thin polished Ebonite Sheets can be produced in the press by the following method:

The ebonite sheet, say 1 mm. thick, is calendered between two tin sheets. As many such sheets as required are placed one on the top of another to fill a frame similar in size to the size of the various sheets in their tin envelope. The press is then closed and the ebonite cured at a given temperature.

When vulcanisation is complete, the tin envelopes are quickly removed from the sheets, the latter then turning black by coming into contact with air. The ebonite sheets get perfectly polished due to their close contact with the tin envelope. Such sheets, after they have been perforated with a special punching machine, can be used as *battery-case-separators.*

CHAPTER XI.

Coating of Iron Rollers with Rubber.

THE task of coating iron rollers with rubber is indeed very difficult. The rollers in most cases are very heavy and they are covered with rubber for multiple purposes. For doing this work satisfactorily, skilled and experienced hands are absolutely necessary. That part of the factory, where the covering or re-covering work is done must be free from dust and not far from the vulcanising section. It should not be exposed to the direct rays of the sun. In cold countries, the temperature of such a place is recommended to be at about 18° C., but this question does not arise in the case of factories located in the Tropics.

Lifting tackles for easy handling of the rollers and solid iron or wooden frames for supporting the rollers are indispensable. Ample space should be provided in this room to enable the workmen to move about freely.

Rollers usually are of either solid cast iron or hollow wrought iron cores. Solid cast iron cores do not allow the rubber coating to vulcanise properly, and for this reason rubber manufacturers are not very keen on undertaking the work of re-covering such rollers with rubber.

The first process connected with the coating of rollers with rubber is to cut grooves on them with a flat chisel. These grooves will help the rubber to adhere firmly to the iron core. This is only a mere precaution, as it sometimes happens that rubber coating on rollers come loose after a few days' work and run off the core in the shape of a gigantic cylinder!

The second process is to clean the surface of the core, so that all dirt and rust may be removed, and to heat the core in order to remove all moisture that may be present on the roller. This can be done by connecting the core (if it is hollow) to a steam pipe. If any pores are found in the core, they should be plugged or filled with lead, so that no blisters may form in the rubber when coated.

The third process is to wash the core with benzine, which is followed by the repeated application of a hard-rubber-solution, care being taken that one coat of solution is completely dry before applying another.

The layer of rubber to be placed first upon the coat of solution must be of a hard composition and must bind closely round the core. Upon this layer of hard rubber, or ebonite, the outer layers are placed, the quality of which will depend on the purpose for which the roller is intended.

The outer layer should be built from a single sheet of not more than 2 mm. thick. The various sheets to form that single sheet are to be well rolled and their edges well pressed together. Care should be taken that the sheet is absolutely free from blisters. If any bubbles appear, they should be pricked with a sharp pin point. As a precaution, each layer, when laid on the other, should be pricked all over and the whole surface wetted with benzine to ensure complete adhesion between the various layers of rubber.

When the core has been completely covered with rubber and the required outer diameter obtained (which may be exceeded by about 2 mm. to allow for the finishing work on the lathe), a paper covered iron flange equal in size to the external diameter of the coating is placed on either end of the rubber coated roller. Then the roller is wrapped in closely woven wet cotton fabric, free of starch, and capable of standing great strain, the weft and warp being of the same quality of yarn.

The wrapping is first done with the fabric thoroughly wetted and placed tightly lengthwise, from one end of the roller to the other, whereupon other cotton straps, also wetted, are placed in spirals, one layer crossing the other, four or five such layers being necessary. The work of wrapping should be done mechanically, if the connection with the installation is not too complicated. The only other practical way is to have a strong handle on either side of the core and to have three or four men to turn the roller until the wrapping is completed.

Then the core is placed on a special carriage, which is introduced into the vulcaniser. After cure, the roller is unwrapped and put on the lathe for the final finishing.

Below are some formulas for different coatings with their relative vulcanisation:

For Printing Rollers:

(a) *Ebonite Base:*

Smoked Sheets	10^{k} 000
Reclaimed Rubber	10^{k} 000
Ebonite Dust	5^{k} 000
Silicious Chalk	7^{k} 500
Sulphur	7^{k} 500
Linseed Oil	0^{k} 300
Carbonate of Magnesia	1^{k} 500
Vulkazit CT	0^{k} 200

(b) *Soft Rubber Coating:*

Crepe	5^{k} 000
Smoked Sheets	5^{k} 000
Zinc Oxide Active	1^{k} 200
Factice F-10 (Grandel)	7^{k} 000

Aldolal Powder	....	0k 120
Sulphur	....	0k 600
Vulkazit CT	....	0k 090

Cure: 1 hour at 120° C.
1 hour at 129° C.
2 hours at 138° C.

The time of curing stated applies to medium size rollers. With larger sizes, the vulcanisation temperature should be increased proportionately.

The following is a mix used for printing rollers, when accelerators were not available:

Rubber	....	2k 500
White Factice	....	1k 750
Zinc Oxide	....	0k 300
Sulphur	....	0k 340

Cure: 2 hours 10 minutes at 280° F.

Ebonite Rollers. For rollers which are exposed to comparatively high working temperatures, the following mixes are used with a high point of softening. The compounds should be well cured. After raising the curing temprature correspondingly (quite apart from the thickness of the coating and the form and size of the iron core), the vulcanisation should take place in about 4 to 6 hours at 304° F.

Smoked Sheets	....	10k 000
Silicious Chalk	....	10k 000
Heavy Carbonate of Magnesia		1k 000
Linseed Oil	....	0k 300
Sulphur	....	4k 500
Vulkazit CT	....	0k 200

Smoked Sheets	....	10k 000
Silicious Chalk	....	5k 000
Mica Dustex	....	5k 000

Heavy Carbonate of Magnesia	1^{k} 000
Linseed Oil	0^{k} 300
Sulphur	4^{k} 500
Vulkazit CT	0^{k} 200

Textile Dyeing Rollers (for Nipping Rollers):

(a) The iron core is coated with the following solution:

Smoked Sheets	10^{k} 000
Zinc White	10^{k} 000
Sulphur	3^{k} 000

(b) The ebonite coated upon the solution is as follows:

Smoked Sheets	10^{k} 000
Ebonite Dust	4^{k} 000
Silicious Chalk	4^{k} 000
Sulphur	4^{k} 000
Linseed Oil	0^{k} 300
Carbonate of Magnesia	1^{k} 000
Vulkazit CT	0^{k} 180

(c) The *soft top rubber* is from the following mix:

Pale Crepe	10^{k} 000
Silicious Chalk	10^{k} 000
Zinc Oxide Special	1^{k} 000
Lithopone	2^{k} 000
Paraffin Wax	0^{k} 100
Stearic Acid	0^{k} 050
Mineral Oil	0^{k} 200
Sulphur	0^{k} 350
Vulkazit H	0^{k} 030
Vulkazit D	0^{k} 030
Aldolal Powder	0^{k} 030
Zinc Oxide Active	2^{k} 000

The stock cures in about 90 minutes at 289° F. In order to vulcanise the thick coating thoroughly, the following cure should be applied in the case of a hollow core:

1 hour	at	120° C.
1 hour	at	130° C.
70 mins.	at	143° C.

The exact cure should be fixed after trials at the Works.

Roller-Coating for Paper Machines:

The following are indications for the processing of stocks for Roller coatings for the production of a medium hard mix.

The sandblasted iron core is coated several times with a rubber solution produced by dissolving a mixture of

Smoked Sheets	....	100^k 000
Zinc White	....	100^k 000
Sulphur	....	30^k 000

in petrol. After the solvent has evaporated, the roller is coated with an ebonite mixture of the following composition:

Sheets	....	100^k 000
Ebonite Dust	....	40^k 000
Clay or Chalk	....	40^k 000
Sulphur	....	40^k 000
Linseed Oil	....	3^k 000
Magnesia Usta	....	10^k 000
Vulkazit CT	....	1^k 800

The soft rubber mix is spread upon the ebonite coating. The sheets must be drawn free from blisters and smooth on the calender, it being necessary to avoid air traps.

A roller coating of a shore hardness of about 63° is produced by the following mix:

Smoked Sheets	....	50^k 000
Zinc White RS	....	80^k 000

Brown Crepe	50^{k} 000
Zinc Oxide Active	20^{k} 000
Oil Black	3^{k} 000
Silicious Chalk	40^{k} 000
Tackol	1^{k} 000
Stearic Acid	1^{k} 000
Phenylbetanaphthylamine	1^{k} 500
Sulphur	6^{k} 000
Vulkazit FP	0^{k} 500

The curing depends upon the measurements of the iron core and the thickness of the rubber coating. The cure for a medium size roller, coated with about 25/30 mm. rubber is about:

1½ hour at 110° C.
1 hour rise to 120° C.
1½ hour at 120° C.
1 hour at 128° C.
1½ hour at 135° C.
1½ hour to 2 hours at 138° C.

Below are two mixes for *Typewriter Rollers*:

1.	Smoked Sheets	10^{k} 000
	Elastic Carbon Black	9^{k} 000
	Kaolin	12^{k} 000
	Sulphur	0^{k} 700
	Vulkazit F	0^{k} 200
	Zinc Oxide	3^{k} 000
	Rosin Oil	0^{k} 250
	Rosin Powder	0^{k} 250
	Aldolal Powder	0^{k} 150

Cure: Rise 15 minutes and maintain 25 to 30 minutes at 304° F.

2.	Smoked Sheets	2^{k} 500
	Carbon Black P 33	2^{k} 250
	Kaolin	3^{k} 000

Sulphur	0^{k} 175
Ureka	0^{k} 050
Zinc Oxide	0^{k} 750
Rosin Oil	0^{k} 063
Rosin Powder	0^{k} 063
Flectol H	0^{k} 031

Cure: rise 15 minutes and maintain 30 minutes at 304° F.

Hard Wet Press-Roller stock for Paper Machines:

A. The iron core is coated with the following solution:

Sheets	10^{k} 000
Zinc Oxide	14^{k} 000
Sulphur	2^{k} 000
Silicious Chalk	4^{k} 000
Vulkazit DM	0^{k} 300

B. The following mix is coated upon the solution:

Sheets	10^{k} 000
Ebonite Dust	4^{k} 000
Kaolin	4^{k} 000
Sulphur	3^{k} 800
Linseed Oil	0^{k} 300
Vulkazit CT	0^{k} 180
Light Carbonate of Magnesia	1^{k} 000

C. The upper ebonite coat is obtained from the following mix:

Smoked Sheets	10^{k} 000
Zinc Oxide	15^{k} 000
Cumaron Rosin	0^{k} 250
Pine Tar	0^{k} 150
Sulphur	2^{k} 500
Phenylbetanaphthylamine	0^{k} 100
Vulkazit FP	0^{k} 060

Cure as follows:

2 hours at 110° C.
1 hour rising to 120° C.
3 hours maintaining at 120° C.
1 hour rising to 127° C.
19 hours maintaining at 127° C.

With a vulcanisation of this kind, one obtains a uniform heating through the whole body of the roller, and at the same time a uniform degree of hardness, which is what the paper manufacturer would like. But it may happen that the pressure of the vulcanisation at the start is not enough to drive out the air located between the wrapping layers of fabric, with the result that the rubber coating may become porous. To avoid this, first inflate the vulcaniser with cold air pressure of about 2½ atm., after which the vulcanisation may be started as explained.

The following are two mixes of special quality for re-covering paper mill rollers with red or black ebonite:

A.	Crepe or Sheets	10^{k} 000
	Zinc Oxide Red Seal	8^{k} 000
	Zinc Oxide Active	2^{k} 000
	Silicious Chalk	5^{k} 000
	Stearic Acid	0^{k} 100
	Red Iron Oxide 720	0^{k} 150
	Phenylbetanaphthylamine	0^{k} 100
	Sulphur	0^{k} 400
	Vulkazit D	0^{k} 035
	Vulkazit H	0^{k} 035
B.	Sheets or Crepe	10^{k} 000
	Zinc Oxide	8^{k} 000
	Zinc Oxide Active	2^{k} 000
	Carbonate of Magnesia	4^{k} 000
	Stearic Acid	0^{k} 100

Red Iron Oxide 720		0^k 150
Phenylbetanaphthylamine		0^k 100
Sulphur	....	0^k 500
Vulkazit FP	....	0^k 050

Black mixes are obtained with the addition of either active or non-active Carbon Black, in place of the 0^k 150 Red Iron Oxide.

The vulcanisation of big paper mill rollers is carried out as follows:

For 5 hours slow uniform rise to 130° C.
then 2 hours maintaining at 130° C., and
further 2 hours maintaining at 138° C.

Lining Iron Tanks with Ebonite. The area to be coated with rubber is sandblasted. The tanks so prepared are immediately coated two to three times with a rubber solution which is prepared from the following mix:

Sheets	....	10^k 000
Silicious Chalk	....	4^k 000
Zinc White	....	14^k 000
Sulphur	....	2^k 000
Vulkazit DM	....	0^k 300

The uncured ebonite sheets are spread on the inside wall of the tank, care being taken that the seams are absolutely tight. The seams must be varnished over. It is advantageous that the edges of the sheets should be rounded. When the tank is thus covered with ebonite, steam is allowed in it for the cure, which is done with a short rise for one hour at 143° C. After that time the vulcanisation is interrupted, so that faulty places such as blisters etc., if any, may be repaired, after which the cure is continued for another 3 hours at 143° C.

1. For a lining of normal strength, not for swelling substances such as petrol, benzine, nitrobenzine, etc. and chemically very active agents such as Chlorine, Hypochlorite of soda etc., the following mix is recommended:

Smoked Sheets	20^{k} 000
Ebonite Dust	8^{k} 000
China Clay	8^{k} 000
Linseed Oil	0^{k} 600
Vulkazit FP	0^{k} 300
Sulphur	7^{k} 200

2. For linings which are chemically highly strained:

Smoked Sheets	20^{k} 000
Ebonite Dust	4^{k} 000
Sulphur	6^{k} 000
Vulkazit FP	0^{k} 500

Ebonite Dust is a finely ground mix of very low ash content.

The curing with Vulkazit FP takes slightly longer than with Vulkazit DM.

Other degrees of hardness may be produced by changing the fillers. By exchanging the silicious chalk, for instance, for the same quantity of Carbonate of Magnesia, the hardness is increased. Oil Black is very suitable for the production of *hard roller stocks.*

CHAPTER XII.

Sponge Rubber.

IN sponge manufacture, there is always some difficulty, and even confusion at times, as to which material or which combination of materials is to be used as a sponging agent. The most commonly used agents at the present time are Sodium Bicarbonate and Ammonium Carbonate.

A usual difficulty is the question of good dispersion of the sponging agent, particularly Ammonium Carbonate. This material has a tendency to cake on standing, and this frequently causes trouble. When using Sodium Bicarbonate on the other hand, it is necessary to use either oleic acid or stearic acid in order to free the gas. This explains the loss of gas on standing, particularly from the surface of the stocks, since the reaction will take place slowly even at room temperatures. Moreover, in hot climates the trouble becomes more serious to combat, and frequently, it is necessary to give up this method of gassing, in favour of a return to the use of the ammonium compound.

Commercial ammonium carbonate is not what may be called a simple chemical entity. The material which is originally pure will, upon exposure to air, rapidly give off ammonia, and will be affected by the moisture of the air, so that ordinary commercial ammonium carbonate is likely to contain ammonium carbamate, ammonium bicarbonate and free ammonia, in addition to the normal ammonium carbonate.

Thus, the effectiveness of commercial ammonium carbonate is liable to vary considerably from batch to batch.

The ideal material to use for the purpose is one which will give the largest possible blow, per unit weight, and one which will disperse uniformly without any special precautions. At the same time, the sponging agent should preferably be without action until above mill temperature, but should gas freely well *below* vulcanisation temperature, in order that the stock may expand thoroughly before vulcanisation begins.

This was the problem in response to which many sponging agents were found and tried, for instance the use of polymerised aldehydes, the use of gaseous pressure in the vulcaniser, i.e. high pressure nitrogen, more volatile non-aqueous liquids, such as various alcohols, esters and the like, but all these are not used as a general rule in practical factory work on account of their not being entirely suitable for all Works.

The best sponging agent finally found satisfactory was the sponge paste offered by the Monsanto Laboratories. This product is a uniform blend of materials ground in a light mineral oil to give the consistency of a smooth cream, such as ordinary petrolatum, capable of giving the best and most economical blow.

The best results have been obtained by the use of 10% sponge paste calculated on the rubber content. But it is difficult to give the exact quantity to be used, since it is entirely dependent on the type of sponge rubber desired, the size of the mould, if curing is done in the press, and the type of rubber stock used. If a small blow of the size of a pinhole is desired, it is probable that 5 to 8% will give the desired result, and consequently for larger blows a greater quantity of sponge paste should be added.

The following formula is recommended by Monsanto as a suitable mix for sponge work, for upholstery of chairs and the like:

Twice masticated rubber	10^{k} 000
Zinc Oxide	1^{k} 000
Golden Antimony	0^{k} 500
Sulphur	0^{k} 400
Cycline Oil	0^{k} 800
Dark Brown Factice	1^{k} 200
Magnesium Carbonate	0^{k} 300
Ureka White	0^{k} 075
Sponge Paste	1^{k} 000
Flectol H	0^{k} 200

The cure for this stock should be about 15 minutes at 105° C. and then 40 to 50 minutes at 141° C.

Monsanto explain that in sponge rubber manufacture of this nature, especially when a large surface of rubber is exposed to the air and is thus liable to oxidation, it is very necessary to protect this surface by the addition of a suitable anti-oxidant. Furthermore, it is desirable to add considerably more than is normally used in rubber manufacture on account of the greater tendency towards deterioration and on account of the fact that the sponge itself is generally supposed to last a good number of years.

It should also be noted that with the above stock, a sponge is obtained which is relatively stiff. This is desirable for this type of product so far as the upholstery business is concerned. For other sponges such as the softer fluffy and bath sponge types, it is necessary to use somewhat more sponge paste and practically no accelerator, also less zinc oxide and no magnesium carbonite at all. Furthermore, very much less stock is used in the mould, and the blow allowed to be much greater by having a very much longer rise period. The resultant product will then be of very much softer feel, and have much larger holes.

Below we give a mix for *sponge mats* with Vulkazit F:

Crepe twice masticated	10^{k} 000
Zinc Oxide	0^{k} 500
Sulphur	0^{k} 250
Silicious Chalk	2^{k} 000
Stearic Acid	0^{k} 400
Cycline Oil	0^{k} 600
Petroleum (rock oil)	0^{k} 500
Vulkazit F	0^{k} 100
Flectol H	0^{k} 100
Sponge Paste	1^{k} 000
Dye ...	-

Cure: 30 minutes at 105° C. and 30 minutes at 142° C.

In the case of thin sponge sheets, the prolongation of the time of cure, which is advantageous for producing uniform holes, is not necessary, and the time of vulcanisation can be reduced to 20 to 26 minutes at 139° C.

The mix is drawn in sheets about 2 mm. thick, powdered with talc and vulcanised in the press between fabrics in a 4 mm. high frame.

Another *sponge mix* is as follows:

Twice masticated rubber	10^{k} 000
Zinc Oxide	1^{k} 000
Stearic Acid	0^{k} 300
Sulphur	0^{k} 375
Brown Factice	0^{k} 800
Cycline Oil	1^{k} 000
Ureka White	0^{k} 150
Sponge Paste	1^{k} 000
Flectol H	0^{k} 100
Dye	-

Cure: 15 minutes at 105° C. and then 20 minutes at 145° C.

CHAPTER XIII.

Insulated Wires and Cables.

THERE is an indisputable connection between the Rubber Industry and the Industry for insulating Wires and Cables, so much so that they can be called *Sister Industries.* Mixing Rollers, Calenders, Forcing Machines and Vulcanisers are common to both of them. Much can be said on the insulation of wires and cables, and we propose to write a separate book on this subject in the near future. In this chapter our intention is to discuss briefly only a few aspects of this interesting fabrication.

First of all a few points are to be noted regarding the mixes needed for insulating wires and cables.

The rubber should be well washed and cleaned. All fillers, i. e. Zinc Oxide, Talc, Kaolin, Whiting etc. should be well dried and sifted to prevent the formation of grains in the insulating sheet, as they will create holes and thereby bad insulation.

Very thin sheets, often of only 0.2 mm., are drawn on the calender, which should have not less than four bowls for this purpose, and blisters should be carefully removed from the sheets. The canvas should also be proofed with care, the rubber coating being smooth and free from granules or any impurities.

The above deals only with the preparation of the insulating material.

Let us now see how wires and cables are insulated. It may be stated, however, that in this chapter no mention is made about the special fabrication of Armoured Cables for under-ground and submarine connections.

The electrolytic copper is drawn on complicated Drawing Machines, capable of reducing ingots into wires as thin as 0.1 m. m. in diameter.

We know already that contact with copper is a cause of deterioration to rubber, as it causes oxidation of the compounds and thereby premature destruction. For this reason copper wires which come into contact with rubber *will have to be tinned.*

Electrical conductors are of simple wires or of combined wires called *cables.* These are produced on Stranding Machines of the *triple tandem type* of English make. Cables are made of 1 + 6 wires, the single wire being the core of the cable, the six others being strands round the core. This is done on the first part of the Triple Tandem Stranding Machine. The cable then passes through the second part of the Machine, where a multiple of six, say 12 bobbins turn in a reverse direction to the first part. These provide a second layer of 12 wires over the first seven. The cable then finally passes through the third part of the machine, turning in the same direction as the first part, where again a multiple of 6, say 18 bobbins cover the cable with a third layer of 18 wires. The cable now consists of three layers with a total of 37 wires. When more wires are required in the construction of the cable, this may be obtained by passing the cable a second time through the triple tandem machine, this time 24 wires to be laid round the cable. It often happens that wires are not of the required length, in which case the ends are soldered together with silver soldering. Wires, or cables, prepared as above are insulated on the Forcing Machine in case the insulation is for 300 megohms, or on the Longitudinal Machine by means of which 3 layers of rubber can be laid upon the wires in one operation. Longitudinal

Machines are of English, French or German make, but in our opinion the English Machine from Messrs. Johnston & Philips is the best, because the grooved rollers together with axle and gear wheel form a single whole.

For insulating the wires on the Longitudinal Machine, the thin sheeted rubber compound is rolled into coils and cut into discs of a given width on an automatic lathe.

Three pairs of rollers are the main parts of the Longitudinal Machine. The wires or conductors are fed through each pair of these rollers between two ribbons of the coiled rubber sheet cut into discs, semi-circular grooves in each roller forcing the rubber to cover the wires, thus forming a circular tube round the conductors. The excess rubber is cut off, the pressure at the joint being sufficient to make the freshly cut rubber adhere.

Twelve wires are insulated in one operation on the Longitudinal Machine which is capable of insulating 24,000 yds. in 8 hours.

For insulating wires for an electrical resistance of 1200 megohms, the para sheet is laid upon the wires through the first pair of grooved rollers, a layer of white rubber compound through the second pair, and a layer of black rubber compound through the third pair. In the case of wires insulated for an electrical resistance of 600 megohms only white and black compounds are applied upon the wire, whereas for 300 megohms, one layer of black rubber compound only is used.

The 12 insulated wires are automatically wound up on 12 take-off drums placed in front of the Longitudinal Machine. From there they are taped on the Taping Machine with the rubberised coiled canvas cut into discs on an automatic lathe as in the case of the rubber sheet. The conductors are spirally taped with the proofed canvas tape in such a way that there is a slight overlap, and a uniform covering. They are collected on winding-up-drums situated at the rear of the Taping Machine. Now the winding-up-drums either from the Forcing Machine, the Longitudinal Machine or the Taping Machine, are placed in the steam-jacketted vulcanising pan. By this operation the cotton tape gets vulcanised tight on the rubber-covered wires, and from that time the rubber-insulated wires gains their elastic character. The most suitable time and temperature for the cure vary with the use of different vulcanising compounds, fillers and accelerators. It is advisable to keep both the time and the temperature as low as possible.

It may be mentioned here that the running-off-drums of the Forcing Machine, the Longitudinal Machine and the run-off and winding-up-drums of the Taping Machine are those which serve in the vulcaniser as vulcanising drums. They are made of galvanised iron, perforated, and being of a special design, a duplication of drums is saved by this method.

After vulcanisation, the wires are put on the winding device, which is used for winding off the vulcanised conductors from the vulcanising drums and winding up on the running-off-drums of the Braiding Machines.

On the Braiding Machines the insulated and vulcanised taped wires are covered with cotton yarn and are then impregnated.

The impregnating plant is provided with two impregnating tanks. In the first is a compound of of bitumen combined with ozokerite and paraffin, raised to a high temperature, so that it thoroughly soaks into the braided conductor. In the second the mixture is at a much lower temperature, immersion in which gives the conductor a very smooth and polished appearance.

The finished wire can now be measured. This is done on the *Length measuring and coiling table*, and according to their different uses, the insulated conductors are coiled in the required lengths ready for sale.

Flexible wires are manufactured on the Bunching Machine, the core of which consists of several tinned copper wires of 0.2 mm. diameter—sometime 100 and more. It may be remarked that bunching is not proper stranding as done on the Stranding Machine. The cores so bunched are insulated like other wires either on the Forcing Machine (for 300 megohms) or on the Longitudinal Machine (for 600 megohms and above). Then they are vulcanised without rubberised tape and then braided with glazed cotton yarn. Afterwards they are twined on the Twining Machine and coiled to be ready for despatch.

A cable factory must possess an electric-high-tension testing plant in which the finished wires or cables can be electrically tested so as to ascertain whether the various items of the fabrication have been properly carried out.

The following are a few *mixes for insulating wires & cables:*

A. With Vulkazit F.

Pale Crepe	....	10^{k} 000
Zinc Oxide	....	1^{k} 000
Whiting	....	12^{k} 500
Sulphur	....	0^{k} 250
Paraffin Wax	....	0^{k} 300
Chalk	....	4^{k} 000

Stearic Acid	0^{k} 050
Vulkazit F	0^{k} 070

Cure: 20 minutes at 132.8° C.

B. With DPG.

Pale Crepe	10^{k} 000
Zinc Oxide	1^{k} 000
Whiting	12^{k} 500
Sulphur	0^{k} 300
Paraffin Wax	0^{k} 300
Chalk	4^{k} 000
Stearic Acid	0^{k} 050
DPG	0^{k} 100

Cure: 20 minutes at 142.8° C.

C. With Vulkazit DM 33½% of Raw Rubber.

Pale Crepe	10^{k} 000
Zinc Oxide	1^{k} 000
Chalk	14^{k} 000
Talc	4^{k} 300
Paraffin Wax	0^{k} 300
Sulphur	0^{k} 300
Stearic Acid	0^{k} 100
Vulkazit DM	0^{k} 060

Cure: 20 minutes at 143° C.

D. With Vulkazit DM 25% of Raw Rubber.

Pale Crepe	10^{k} 000
Zinc Oxide	1^{k} 000
Chalk	23^{k} 900
Talc	4^{k} 300
Paraffin Wax	0^{k} 400
Sulphur	0^{k} 300
Stearic Acid	0^{k} 100
Vulkazit DM	0^{k} 060

Cure: 20 minutes at 143° C.

Remark: There is more to be said about this very important fabrication of insulating wires and cables, which cannot find its place in the frame of this publication.

CHAPTER XIV.

Miscellaneous.

MOULDED goods are of solid or hollow structure. The solid ones are articles with metal, wood or fabric cores, *Ball Valves*, for example, which are made in the following manner, in order to prevent the core changing its place in the centre.

The core on which the article is to be built up is well roughened and painted with a thick layer of solution on which, after the solvent has evaporated, calendered sheets cut in ∞-shaped pieces are placed, so that they completely cover the ball. The cut edges are washed with a solvent and well pressed together. This process is repeated with other ∞-shaped rubber pieces until the desired diameter of the ball is obtained. Care should be taken to see that the edges of the ∞-shaped pieces are not placed one on the top of another but slightly overlapping. The ball thus produced has now as spherical a shape as possible. After a preliminary pressing in the mould to ascertain that it is completely filled with rubber, the mould is firmly clamped with strong nuts and bolts, and introduced into the vulcanising pan where it is cured.

Smaller balls may be obtained in a different way: by winding narrow strips of sheet round the core. With this method, it often happens that, owing to irregular winding, the core may be shifted from the centre.

For the manufacture of *Bottle Stoppers*, suitable cord is extruded on the Forcing Machine, and cut into sections of the required weight, then they are pressed into moulds to be cured.

With moulded goods it is necessary in all cases first to determine the exact weight of the article to be made, to which 2 to 3% is to be added for press-waste. With all moulded goods, care must be taken to see that sheets and cords drawn either on the Calender or on the Forcing Machine are free from air-holes in order to avoid producing faulty articles.

Whilst small moulds are securely closed by strongly bolted iron clamps and so exposed to high pressure to be cured in the vulcaniser, other moulded goods, such as billiard strip, deckle straps, pulsometer valves and the like are subjected to high pressure while they are under the vulcanising press.

With articles delivered in great lengths, such as deckle straps, billiard strip, moulded cord, garry and rickshaw tyres, beltings etc , vulcanisation has to be carried out in sections. It is therefore absolutely essential for the mould to protrude about 8 inches from both ends of the press.

When vulcanising the first length, the head-end of the mould is closed and only one end protrudes under the press. During subsequent vulcanisation, the head plate is screwed off the mould and both ends are permitted to protrude, so that in due course the vulcanised part can leave the mould. But in order that the succeeding unvulcanised rubber may not be displaced, the completed part emerging from the mould must be well tied down, whereby a running movement is prevented.

Deckle Straps are produced in the same manner. Then their ends well bevelled and washed with a solvent are brought together and vulcanised in a small mould of the same shape, thus rendering the strap endless. As explained already in a previous chapter, air-markings may appear if the mould is not tight enough or if the air does not find an easy outlet; also when opening the mould, the lid should not be taken off quickly enough to create a vacuum between the rubber and the mould, owing to the cooling down of the rubber compound. It may be remarked that inferior, soft, and over-milled rubber compounds cause air-marks.

Another way of producing deckle straps, without moulding is as follows:

The required compound is calendered into sheets of about 2 mm. thick, which are doubled, so as to attain the specified thickness. The sheet is then placed round a cylindrical drum well wrapped in fabric and allowed to remain in boiling water for 5 to 10 minutes. After the mix has been cooled down, the sheet-cylinder is removed from the drum and cut spirally in straps of the required length and width. After both the ends have been bevelled and washed with a solvent, they are joined and the deckle strap is vulcanised in talc in open steam. Vulcanisation being completed, the four faces of the deckle strap are buffed on the grinding stone and the article is ready to be packed for despatch.

The following is a *mix for deckle-straps:*

Smoked Sheets	....	10^k 000
Sulphate of Barytes		8^k 000
Silicious Chalk	....	2^k 000
Stearic Acid	....	0^k 050
Ozokerite	....	0^k 150
Zinc Oxide	....	0^k 500
Cycline Oil	....	0^k 300
Sulphur	....	0^k 200
Vulkazit F	....	0^k 100

The mix can be cured in 8 minutes at 151° C., but, to obtain a satisfactory vulcanisation without porosity inside the cured article, it is recommended to carry out the cure at comparatively low temperature for a longer period. We suggest a cure temperature of 127° C. As for the time, this should be ascertained by local factory tests.

The second class of moulded goods consists of *hollow articles* either built up on a mandrel forming the interior or, as in the case of balls, dolls and animal shapes, expanded by gas. In both cases the articles are built up of cut out sections of sheet. The manufacture is mainly done by hand. With rubber balls, the various segments are cut or punched by machine. Balls are usually made up of four to six pieces, which are joined after washing the edges with a solvent, and well pressed together.

In the case of balls, a plug of rubber compound without sulphur and accelerator is placed somewhere on the inside of one of the .segments, the object of which will be explained later on. Before the last segment is closed up, a certain quantity of carbonate of ammonia say from 8 to 40 grams, according to the size of the ball and the stretching capacity of the rubber compound, is introduced into the ball.

There are other processes for blowing out balls based on the principle of introducing into the ball substance developing nitrogen. But a process, however, which would simplify the present method of manufacture and which would render the plug and the filling of balls with nitrogen after vulcanisation unnecessary, has not so far been developed.

Still another process for expanding hollow goods is the use of nitrite of ammonium, which under the action of heat is decomposed into nitrogen and water according to the formula:

$$NH_4\,NO_2 \quad = \quad 2\,H_2O + N_2$$

Nitrite of ammonia may be produced in the ball itself by the combined action of nitrites of alkalis and chloride of ammonium.

It is also advisable to develop carbonic acid from bicarbonate of salts. Nitrogen may be produced from chloride of lime and ammonia, and instead of the latter, carbonate of ammonia may also be used.

If the mix is not properly composed, and especially if it is not homogeneous, i. e. if the micro-porosity of the rubber is too great, the ammonia easily penetrates the wall or fills the pores of the rubber, thus causing it to perish. In such circumstances, crystals of ammonia are formed on the outside of the ball, permitting gases and air to escape. To avoid this, it is advisable to add to the compound a certain quantity of mineral and reclaimed rubber. It may be that the compound will be somewhat dark, but this does not much matter when balls are to be supplied painted.

Now-a-days ready made *inflation tablets* are supplied by Messrs. Allen and Hanburys Ltd., London.

Sodium Nitrate can also be used for the same purpose. According to experience gained by the author, *ammonium chloride* with a few drops of water should be used for inflating rubber goods which are vulcanised in *steel moulds* whereas *ammonium sulphate* with a few drops of water is to be used for inflating goods cured *in aluminium moulds.*

Toys such as dolls and animals are manufactured just like balls and they are best inflated by introducing into the goods to be vulcanised one or two inflating tablets. The cure of the goods should be done rising for 2 minutes at 110° C, then as quickly as possible at the stipulated temperature. When vulcanised, the moulds, after being thoroughly cooled down, are opened. This can be done safely as the gases by now have no further expanding power and their volume has been reduced by the influence of the cold. Then the ball is filled with compressed air. This is done by passing an air needle through the unvulcanised plug which, it will be remembered, has been placed inside the ball and which contains neither sulphur nor accelerator. When the air needle is removed, the pressure inside the ball causes the soft rubber of the plug to close up the little channel made by the needle, so that the air cannot escape.

It is advisable to cover the outside mark produced by the needle by applying solution to it, but this is only to give a neater appearance.

Dolls and animals after being vulcanised need not be inflated as they are fitted with air-valves inserted in the finished article.

The following is a *mix for balls:*

Smoked Sheets	10^{k} 000
Zinc Oxide Special	0^{k} 800
Sulphur	0^{k} 300
Gloria Factice	1^{k} 000
Stearic Acid	0^{k} 060
Vulkazit F	0^{k} 090
Silicious Chalk	12^{k} 000
Kaolin	4^{k} 000
Lithopone	2^{k} 000
Rosin Oil	0^{k} 150
Paraffin Wax	0^{k} 200
Mineral Rubber, if found necessary	1^{k} 000

Cure in mould: Rise for 2 minutes at 110° C., then 15 minutes at 148° C.

The following is a *mix for Dolls,* animals and the like:

Pale Crepe or smoked sheets	10^{k} 000
Zinc Oxide Special	0^{k} 500

Sulphur	0^{k} 220
Vulkazit F	0^{k} 080
Silicious Chalk	6^{k} 000
Cycline Oil	0^{k} 300
Paraffin Wax	0^{k} 050
Acid Stearic	0^{k} 050
Lithopone	0^{k} 150
Mineral Rubber	-
Dyes	-

Cure in press rising for 2 minutes at 110° C., then 15 minutes at 143° C., or 10 minutes at 148° C.

For grey mix, add Mineral Rubber 1^{k} 000

For coloured articles:

Blue—add Vulcan Blue LF	0^{k} 160
Orange—add Vulcan Fast Orange GF	0^{k} 120

The following are *two mixes for (moulded) Tennis Rings.*

A.	Pale crepe	10^{k} 000
	Zinc Oxide Special	0^{k} 500
	Sulphur	0^{k} 220
	Vulkazit F	0^{k} 080
	Silicious Chalk	12^{k} 000
	Cycline Oil	0^{k} 300
	Paraffin Wax	0^{k} 050
	Stearic Acid	0^{k} 050
	Lithopone	0^{k} 150

Dyes as for the above mix.

Cure: 15 minutes at 143° C. or 10 minutes at 148° C.

B.	Pale Crepe	10^{k} 000
	Sulphate of Barytes	8^{k} 000
	Kaolin	2^{k} 000
	Stearic Acid	0^{k} 050
	Paraffin Wax	0^{k} 060
	Zinc Oxide	0^{k} 500

Cycline Oil	0^{k} 300
Sulphur	0^{k} 200
Vulkazit F	0^{k} 100
Lithopone	0^{k} 200

Dyes as per test.

Cure: 8 minutes at 151° C.

Two mixes for moulded *Pessaries and Teats:*

	A 1	*A 2*
Pale Crepe	10^{k} 000	10^{k} 000
Zinc Oxide Active	0^{k} 050	0^{k} 040
Sulphur	0^{k} 020	0^{k} 180
Cycline Oil	0^{k} 100	0^{k} 100
Stearic Acid	0^{k} 050	0^{k} 075
Vulkazit Thiuram	0^{k} 011	0^{k} 030
Vulkazit J	0^{k} 020	-
Vulkazit P	-	0^{k} 015

Cure: A 1, 15 to 20 minutes at 133° C.
A 2, 15 to 20 minutes at 119° C.

Mixes for *Hot Water Bottles* and *Ice Bags:*

A.	Pale Crepe	10^{k} 000
	Zinc Oxide Special	1^{k} 000
	Whiting	5^{k} 000
	Sulphur	0^{k} 110
	Ozokerite	0^{k} 050
	Vukazit F	0^{k} 120
	Vulkazit Thiuram	0^{k} 012
	Dyes	-

Cure: 8 minutes at 147° C.

B.	Crepe	10^{k} 000
	Zinc Oxide	1^{k} 000
	Silicious Chalk	8^{k} 000
	Cycline Oil	0^{k} 200
	Stearic Acid	0^{k} 050
	Sulphur	0^{k} 200

Dye RSL	0^{k} 200
Ureka White	0^{k} 100

Cure in mould: 6 to 8 minutes at 306° F.

Mix for moulded *Bathing Caps:*

Crepe	10^{k} 000
Zinc Oxide	0^{k} 500
Stearic Acid	0^{k} 050
Dye RSL	0^{k} 100
Sulphur	0^{k} 200
Ureka White	0^{k} 100

Cure: 6 to 8 minutes at 306° F.

Mix for *Horn Bulbs:*

Crepe Rubber	10^{k} 000
Zinc Oxide	1^{k} 000
Sulphur	0^{k} 300
Ureka White	0^{k} 150
Dye RSL	0^{k} 125
Stearic Acid	0^{k} 100
Silicious Chalk	15^{k} 000
Lithopone	2^{k} 500
Cycline Oil	0^{k} 400

Articles having an inflating tablet are cured as follows:

2 minutes rising up to 232° F. for allowing the inflating tablet to act, then 6 to 8 minutes at 306° F.

The following is a *retreading stock recommended for motor car tyres:*

Smoked Sheets	10^{k} 000
Zinc Oxide Red Seal	1^{k} 000
Carbon Black Micronex	4^{k} 000
Sulphur	0^{k} 280
Tackol	0^{k} 200

Phenylbetanapthylamine	0^{k} 100
Stearic Acid	0^{k} 250
Vulkazit F	0^{k} 120

Cure in Watch Case:

8 to 10 minutes at 151° C., followed by
15 to 20 minutes at 143° C., terminated by
30 to 40 minutes at 130° C.

The fabrication of *Insulating Tape* is done by the following method. A very fine fabric as wide as possible is rubberised on both sides on the Rubberising Machine, rolled on a cardboard tube of about 1″ diameter, cut in discs of about 12 mm. wide and packed in tin or alluminium sheet.

Black and White Tapes are obtained from the following:

Mix A — Black:

Smoked Sheets	10^{k} 000
*Crepe	2^{k} 500
**Rosin Oil	0^{k} 500
Neutral Wool Grease	1^{k} 500
Mineral Rubber	1^{k} 500
Rosin	2^{k} 000
Adhesive Factice	2^{k} 500
Sulphate of Barytes	40^{k} 000
Aldolal Powder	2^{k} 000
Black Soot P33	5^{k} 000

In order to obtain a somewhat viscous solution, the compound, when mixed on the roller, must be dissolved in the solvent.

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*These should be separately mixed for incorporation into the stock.

**The Rosin Oil should be heated at 180° C. until a highly viscous paste is obtained, which is then mixed with 2^{k} 500 of crepe rubber.

Mix B — Black:

Pale Crepe	10^{k} 000
*Pale Scrap	4^{k} 000
**Rosin Oil	1^{k} 000
Rosin	4^{k} 000
Neutral Wool Grease	2^{k} 000
Gutta-percha Rosin	1^{k} 000
Lithopone	20^{k} 000
Adhesive Factice	2^{k} 000
RR5 Product from I. G.	0^{k} 200

Pure rubber, called *Para - Tape*, is obtained from the following formula:

Smoked Sheets	10^{k} 000
Brown Factice	2^{k} 000
Paraffin Wax	2^{k} 000

The mix is calendered in fine sheets, say about 0.2 mm. thick between fine paper, then rolled on a cardboard tube and cut into discs of about 12 mm. wide. The discs are packed in alluminium sheet and are ready for use.

Fluted Sheetings for motor car footboards are manufactured by the following two methods. Mixes M2 White, Black or coloured (See Part II, chap. VIII) should be used for this fabrication.

1st Method: The compound is calendered in a sheet of about 3 mm. thick, then doubled on one side with a rubberised fabric and vulcanised with the rubber on an engraved plate mould. Such fabrication has two defects:

1. the manufacturing process of long sheets is very slow and therefore the working charges very high.

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*To be mixed separately as in the case of Mix A.

**To obtain viscosity, the mix should be dissolved as in the case of Mix A.

2. for sheets to be manufactured in great lengths the vulcanisation has to be carried out in sections, the end of one section and the beginning of the subsequent section being vulcanised twice, thus giving an overcure to such places, which is detrimental to the quality of the sheets.

2nd Method is better and cheaper and gives a larger daily output. The mix M2 is calendered in a sheet of 3 mm. thick and doubled on one side with a rubberised fabric. The sheet so prepared and well dusted with talc is passed through a two-cylinder-calender, the upper cylinder of which has an engraved surface, against which the rubber sheet is pressed, so that it obtains an impression of the engraved roller on its surface. Then the sheet is wrapped on a wrapping drum especially prepared for that purpose with a mattress of many plies of soft fabric, the engraved rubber side of the sheet facing the mattress. The whole sheet is then rolled round the drum and vulcanised, the last layer being kept in place by a single band of unrubberised fabric. After cure, the sheet is taken off the drum, the design appearing perfectly well, and can be despatched after the borders have been cleaned and trimmed. Such kind of fabrication, needless to say, can only be done by skilled workmen, but is quite possible, as the author has on several occasions produced such sheets in lengths of 10 to 20 meters.

Before concluding this chapter and with it the second part of the book, it may be stated once again that the author agrees with Monsanto and others that the ease with which Ureka White F, the Takars and Vulkazit F mixes can be worked on the Forcing Machine and with which the commencement of the vulcanisation can be adjusted, make these accelerators exceedingly suitable for tubings to be vulcanised in talc in open steam. Short working of the stock on the Mixing Roller, the avoiding of too great a plasticising, the extruding of the stocks at the lowest possible temperature consistent with the obtaining of good smooth surfaces and the cure of tubings with the shortest possible rise are important points in obtaining *round tubings* free from deformation.

A reason for milling the rubber as little as possible is to keep it *tough and nervy*, after it has been extruded or calendered. When preparing the mixes, they should always be dipped in water after milling. Likewise the strap from the tubing machine or calender may need to be water-cooled, and when ultra-accelerators are mixed in the compounds, there is no reason why a certain portion of water should not be added during the milling process; the water not only reduces the temperature on the mixing roller but helps the mastication of the rubber as well. In mixing the stock, either the sulphur or the accelerator, or both, should be added near the end of this operation or better during the warming up of the mix. As regards moulded tubes, in tubing the stocks the pin of the machine should be off centre and should be so adjusted that when the tube is spliced and inflated, the gauge of the stock is relatively uniform. Several hours, or even a day, should elapse after the extruding of the stock and before the vulcanisation, as the handling of soft or warm stocks usually results in uneven expansion. For moulded tubes, it is essential that the mould should be closed after the tube has touched the hot metal. Ordinarily, not more than 10 to 15 seconds is allowed, after the tube touches the hot mould, for the mould to be closed, locked and air turned in to expand the tube. The quicker the mould is operated, the better the results obtained. Air pressure for inflation should always be slightly higher than the steam pressure used for the cure.

Part III.

CHAPTER I.

Latex.

IN Part I of this book, we have spoken of Latex, and we know that, due to bacterial action, this natural product has a tendency to coagulate as soon as it flows from the rubber tree, so if it is to be conserved in its liquid form, the addition of a preservative agent, after tapping is necessary. There are a good many preservative materials but the one generally adopted is ammonia, say 2% on the volume of latex, of a 28% solution.

Ammonia can be added to the latex either in the form of a solution or a gas. The solution is not recommended for the Tropics, gas ammonia being preferable.

Preserved latex differs greatly from fresh latex in its physical and chemical properties. Its viscosity and surface tension are reduced, when preserved, its rate of cure is increased, and on standing for some time degradation of the latex protein takes place accompanied by precipitation of magnesium ammonium phosphate.

Preserved latex often shows considerable sediment which contains not only dirt and sand, incorporated in the course of handling on the plantation, but also insoluble phosphates due to the re-action of ammonia with certain constituents of the natural latex.

Before preserved latex is used by the manufacturer, it should be allowed to stand until most of the sediment has settled down, and the product is then ready for further treatment.

It may be remarked that latex is a *Colloid*, and not a *solution*. The 30 to 40% natural latex and the 58 to 75% concentrated latex is an aqueous dispersion of a relatively labile system, and the many difficulties which occur during its working are the result of its colloidal nature. The first of these difficulties is generally caused by the premature coagulation of the product, due to imperfect wetting, poor dispersion and quick settling of the various ingredients composing the latex mix. Of all the methods considered to give a greater degree of safety to latex processing, that of stabilisation with suitable materials is the most important. No doubt a large number of methods has been suggested for stabilizing purposes: dilution with water, addition of alkalis, soaps, casein and the like, but the action of these is in part insufficient and in part their use is bound up with disadvantages such as frothing, bad ageing, water susceptibility of the latex film etc.

Now before proceeding with the description of these materials, called wetting, stabilizing and dispersing agents, let us consider the ways of obtaining the concentrated latex which is of primary importance in the latex Industry.

We have just said that latex is a *Colloid*. *Colloid* is a name given by Graham, in contradistinction to *Crystalloids*, to any suitable substance which, when exposed to *Dialysis* does not pass through the porous membrane. *Dialysis* is the separation of substances by diffusion through a membranous partition. It is only by examining the latex through a microscope that one is convinced of its colloidal nature, for the rubber particles in suspension in their surrounding liquid are constantly in Brownian Motion,* moving in every imaginable direction the smaller these particles, the more rapid their motion, whereas when these particles have their volume increased, the Brownian Motion is brought to a standstill.

In his *Latex in Industry*, Royce J. Noble writes that not less than fifty million moving particles of rubber can be detected in one cc. of an 8.7% concentrated latex. Any change in the condition of these particles results in some change in their movement. By diluting the latex with from 2 to 3% of a 28% ammonia solution, the Brownian Motion ceases to exist without creating any sort of coagulation. This phenomenon is explained by the fact that ions deposit themselves on the surface of the particles, and their volume is thereby largely increased. Ions, as we all know, are the components into which an electrolyte is broken up on electrolysis, the anion being the component chemically attacking the anode. This can be observed by passing an electric current through the mass of the latex, the particles of which then travel towards the positive electroids, which is the proof that these rubber particles are negatively charged.

Now, if the Brownian Motion is capable of keeping the rubber particles in suspension in ordinary latex, no sooner do ions attach themselves to these particles than the Brownian Motion is stopped, with the result that the rubber particles with their absorbed layer, being now lighter than the aqueous medium in which they are immersed, rise to the surface forming also an

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* *The Brownian Motion* is the movement of the submicroscopical particles and the molecules in a gas and in a liquid. Further detailed explanation of this complicated phenomenon can be found in any text book of Theoretical Physics, particularly in the parts dealing with Statistical Mechanics and Kinetic Theory of Gases.

upper layer which is the concentrated latex. The method by which this is obtained could be called the *Electrical Process.*

Royce J. Noble explains further that, if any other alkali, for instance ammonium hydroxide, is added to the latex, it is ionized in the same way, forming both hydroxyl and ammonium ions. Now the negative hydroxyl ions being more strongly absorbed by the latex particles than the ammonium ions, the addition of an alkali causes an increase in the negative charge of the latex particles. This in turn results in an increased resistance to coagulation of the latex particles, when materials such as acids containing positive hydrogen ions and metal salts such as alum, containing positive aluminium ions, are added to the latex ("Latex in Industry", page 33.)

It was after the Great War that specialists began to devote their energy and knowledge to the discovery of practical methods of concentrating the latex, as the application of rubber in its primitive form was found possible and more useful in a large number of cases. For shipment purposes also, it is more profitable to ship as much concentrated latex as possible, as there is no need to ship the aqueous medium which can be left behind for an equivalent quantity of concentrated latex, thus increasing the profit of both the exporter and the importer.

Various methods of concentrating latex are being worked with success. The *Electrical Process* of which mention has just been made is one of them, the *Creaming System* is another.

Creaming of latex is rendered possible with alkalis and some organic colloids like the *Karaya gum*, the *gum tragacanth* and the *locust bean gum*, which we tried with increasing success. As in the case of ions, these gums are deposited on the surface of the rubber particles in latex. The rubber particles thus increased in volume stop the Brownian Motion, and the particles thus becoming lower in specific gravity rise to the surface.

We have used these gums in the proportion of 1% on the weight of the rubber content in the latex. They are dissolved in distilled water and the solution so obtained is thoroughly stirred into the latex, which is then allowed to stand for 24 hours, after which period latex having not less than 58% of solid rubber will be seen floating on the surface of the liquid medium. The underlayer of almost clear water escapes through a tap fixed at the lower part of the tank made of cypress wood, the concentrated latex then being ready to be mixed with adequate fillers, sulphur and accelerator for further processing as will be explained in the following pages. Royce J. Noble says in *Latex in Industry* that the creaming of the latex can be hastened by heating the liquid at about 60° C.

Concentrated latex floating on the surface of the liquid shows, however, a certain quantity of the creaming material which was incorporated in it, but has a lower content of what is called Serum Solids than was found in the latex before being concentrated. The latex so concentrated can be still further concentrated by stirring in it an additional 0.5% of Karaya gum and so re-creaming it by a similar operation. The latex thus obtained is rich in rubber and its application to the fabrication of various classes of rubber goods is increasing day after day.

As already stated Locust Bean Gum can also be used for the creaming of latex in the same way as Karaya Gum. Royce J. Noble suggests dissolving 15 ℔s. of Locust Bean Gum in 160 ℔s. of hot distilled water and mixing this solution rapidly in 1000 gallons of a 40% latex, allowing the latex so mixed to stand for 24 hours and thus having the concentration as stated above.

It is also suggested that Ammonium Alginate is one of the most effective of the known creaming agents, and by using 0.1% of this chemical, based on the weight of the dry rubber content in the latex, it is easy to obtain a cream having approximately 58% solids and a Serum showing 9% solids.

Another method for concentrating latex is the *Centrifugal process*, introduced by Beffin. He subjected Hevea Latex to centrifugal action in an ordinary milk separator and so obtained a latex cream which he dried out on a porous plate to form a rubber film. This centrifugal operation is almost similar to that of creaming, the only difference being that instead of relying on gravitational forces to cause the lighter particles to rise to the top of the heavier latex serum, the separating force employed being that of centrifugal motion—a force which is several times that of gravitational force (Latex in Industry, page 57).

In short the method employed by Beffin is to pass the already preserved latex through a centrifugal apparatus rotating at about 10,000 R. P. M., which produces a concentration of latex containing about 58% dry rubber and a serum having 9% rubber. As for the recuperation of the rubber contained in the serum it is not quite easy and can only be achieved by chemical reaction, which will coagulate the rubber. This coagulated rubber can no more be used for latex work, but can only be incorporated in mixes as dry rubber.

The *evaporation process* for obtaining concentrated latex is quite different from the creaming process. By evaporation the water only is removed from the latex and as all its other constituents remain, the resultant latex is called the *Whole Latex.* The evaporation method merely consists of heating natural latex at 80 to 90° C. with the addition of glue, potash, soaps or any other stabilizing material, allowing the water to evaporate. But in order to prevent skin formation, it is essential to provide some method of agitation of the latex as the more the latter becomes concentrated, the more difficult will it be to prevent that skin formation.

Another method of concentrating latex by evaporation is to blow hot air on to its surface so that the agitation thus produced may hasten evaporation. But by this process coagulation on the surface is likely to take place as stated above. Hence the use of stabilizers is absolutely necessary.

With regard to *Acid Latex,* its stability is greatly improved by the addition of a suitable protective before acidification. For this purpose casein or certain sulphonated naphtalene derivatives, such as sodium methylene naphtalene, may be employed. Other materials which can be similarly used are gelatine, hemoglobine, saponin, licorice, dextrine and gum tragacanth. Reversal of charge may also be effected by treatment by metal salts.

In practice the stabilising agent is first added to the latex, after which the ammonia is removed or neutralised. This removal is effected by blowing with air or by subjecting the latex to the action of silicate gel or activated carbon. The ammonia may be neutralised instead of removed if substances are added which react to precipitate insoluble hydroxides or form ammonium complexes. As the ammonia is thus removed or neutralised the stabiliser tends to prevent any coagulation. After removal of the ammonia, the latex will have a pH* value of between 7 and 8 and may be treated with any acid material to further decrease the pH value. For this purpose, about 4% of formaldehyde solution may be added, after which it will be found that the pH value has been reduced below 7 and depending upon the amount of formaldehyde added, the pH value may be as low as 4.5.

It has been found that the rubber obtained from acid latex *is more plastic and more adhesive* than rubber from preserved latex. Some advantages of this property have been realised in the preparation of adhesives for impregnating fabrics. Fabrics to be treated with latex should be without *dressing*. The removal of *dressing* from textile fabrics is done by boiling the fabric in a 3% hydrochloric acid solution, then soaking it in a carbonate of soda solution and drying it afterwards.

Below are extracts from reports we have received from Van der Bilt, who recommends the use of his *Age-Rite White* product as a protector against copper contamination and his *Darvan* for improving the quality of dispersion, prevention of settling, frothing, thickening and flocculation.

Copper, says Van der Bilt,—and all of us agree with him—is an enemy of rubber in general and of latex compounds in particular. In fact the deteriorating effect of copper and copper compounds on rubber is well known, and a considerable number of references to this subject are to be found in literature dealing with rubber. While there is usually little likelihood of copper contamination occuring in ordinary dry

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**pH Value* is the negative logarithm of the hydrogen-ion-concentration. The neutral point being approximately 7.1, lower values indicate acid solutions, whereas higher values show alkaline ones.

rubber manufacturing, the chances of such contamination are much greater in latex work. They even constitute a danger to users of latex and one must constantly be on the alert.

Latex and latex products may become contaminated by copper in several ways:

(a) By the use of copper or brass tanks, rollers, stirring devices, or piping in apparatus used for mixing, handling or storing latex. The latex becomes directly contaminated with copper due to the fact that dilute ammoniac solutions readily attack and dissolve metallic copper or brass.

(b) By the use in latex compounding of water containing undue amounts of copper which is the case in some localities where the water supply is treated with small proportions of copper sulphate for purification purposes.

(c) By the presence of copper compounds in textile fabrics which are subsequently rubberised with latex. Textiles frequently have an appreciable copper content. This may come from the use of copper salts as mordants in dyeing processes, from the use of dyes containing a copper nucleus, or from the treatment of dyed fabrics by immersion in copper salt solutions. Copper compounds in the textile and dyeing industries are fairly extensive.

Very small proportions of copper are sufficient to cause rubber goods made from latex to deteriorate rapidly. The effect of copper may not be noticeable in the freshly deposited or freshly cured rubber, but after a while, however, the goods become soft, sticky and resinous.

Fol and *de Visser* have reported a case in which latex-impregrated-fabric, rolled up hot after the calendering process and stored, has quickly developed heat enough to char the fabric and start spontaneous combustion. After investigation, the trouble was traced to the latex used, which had been placed in a brass tank. In conclusion, there may thus be some fire hazard involved as well as the risk of loss through premature deterioration, when copper gets into latex products. As a safeguard, Van der Bilt recommends his *Age Rite White.*

It is a fact that certain age resisters retard the deteriorating action of copper, some more strongly than others. Hence the inclusion of an effective copper-resisting antioxidant in latex compounds is most important, and it so happens that Age Rite White, which is about the best all round antioxidant for latex, says Van der Bilt, has an definite tendency to protect rubber against the deterioration by copper. The addition of about 1 per cent of Age Rite White on the rubber is recommended in most latex recipes.

In connection with improving the Quality of Dispersion and Preventing of Settling, Frothing, Thickening and Flocculation, Van der Bilt says that in making water dispersions of one or more materials, it is not uncommon to encounter trouble from various sources, and these difficulties may appear to be a source of continual trouble, which if the dispersion is carefully examined, can usually be located and the proper remedy applied.

Difficulties due to poor *dispersions* for instance may quite often be reduced or eliminated by the use of one or more of the following methods:

1. Addition of a suspending agent.

2. Addition of an alkali such as Caustic Soda or Ammonia.
3. Addition of a foam reducer.
4. Changing the concentration of the dispersion.
5. Changing the grinding time.

Settling is a trouble that can be practically eliminated. Most dispersions, however, will settle a little no matter how they are made. A small amount of settling is not objectionable as long as the deposit does not become hard. The tendency to settle may be lessened by:

1. Increasing the grinding time, which gives a smaller particle size and therefore the dispersed material will stay better in suspension.
2. Increasing the concentration of the dispersion, which gives a more viscous dispersion and holds the dispersed material in suspension. If the concentration is too high, the dispersion will become a thick paste and will not flow from the mill on completion of the grind.
3. Addition of a suspending agent such as casein will form a protective coating around the dispersed material and prevent it from settling. From 3 to 5% of *casein* on the dispersed material will show a marked improvement in the quality of the dispersion.
4. Addition of an alkali such as Caustic Soda, the effect of which is to prevent a dispersion from settling, dependant upon the pH of the dispersion. In order to make a good dispersion the pH should preferably be above 9. In making dispersions of acid materials a small amount of caustic soda will work

wonders in preventing settling and caking. The following dispersions show the effect of caustic soda:

	A	B
Zinc Oxide....	0.5	0.5
Sulphur	1.0	1.0
Captax	0.5	0.5
Butyl Zimate	0.5	0.5
Age Rite White	0.5	0.5
Darvan	0.12	0.12
Water (distilled)	1.88	1.78
Caustic Soda	-	0.1
	5.0	5.0
Approximate pH value	5	9

Both A and B were ground for 12 hours in a pebble mill, removed and allowed to stand for 50 days without agitation. At the end of that period dispersion "A" had settled rock-hard and could not be removed from the jar. "B" had settled to some extent but could easily be stirred into a uniform dispersion. The latter showed no hard packing at the bottom of the jar.

Frothing is caused by air being beaten in and trapped in the dispersion during the grinding process. In some cases, dispersions will cause no trouble for quite a while and then for no apparent reason will start to froth. *A good remedy for frothing of this kind is to stop the mill for 8 hours or more.* This will usually allow the trapped air to escape and the grinding may be continued. Some materials will always froth when ground in a pebble mill. To eliminate this trouble, Van der Bilt recommends using about 1% on the dispersion of Rodo No. 0 or No. 10. This meterial works very well as an anti-foaming agent and can be added directly to the dispersion in the mill.

Thickening, also called thixotropism, of a dispersion is caused by one or more of the dispersed meterials forming a gel-like structure in the dispersion when it is not being agitated. This gel-like structure causes the despersion to become thick and lose its liquid characteristics. On stirring such a dispersion the gel structure is broken down and the dispersion becomes once more a liquid, but will remain so only as long as it is being stirred. For eliminating this thickening from 3 to 5% of casein should be added to the dispersion.

Flocculation often occurs when the pH of a dispersion is below 7. If a small amount of weak acid is added to a good dispersion, it will spread out and flocculate much faster. This is another reason for adding a small amount of caustic soda to a dispersion in order to keep it alkaline.

Since latex is a water dispersion of rubber, the compounding ingredients which have to be added to it must be added in the form of water dispersions. The success of latex processes and the quality of the goods made therefrom depend to a large extent on the quality of the dispersions used. In making dispersions of compounding ingredients suitable for modern latex compounding practice, two important factors have to be kept in sight, namely:

1. *Good dispersion of the ingredients.*
2. *High concentration of the ingredients.*

The first property makes for good quality, uniformity and good age-resistance in the finished articles, while the second is desirable in order to control the amount of water which is added to the latex and to avoid unnecessary dilution.

Most insoluble dry powders can be mixed directly with water by stirring to form pastes or viscous dispersions. Some are more difficult to mix than others, and a few are so insoluble that no amount of stirring and agitation will cause the water to wet the powder. In such cases if the powder is first moistened with a little alcohol, the water can be made to wet it.

The Water Absorption of Powders, or the ratio of the weight of powder to the weight of water required to form a paste or dispersion of given consistency or viscosity varies enormously for different powders. This ratio depends principally on the nature of the powder and on its particle size.

Some powders, for instance, the various forms of commercial whiting, have low water absorption capacity, and can be readily stirred into thick liquid pastes with considerably less than their own weight of water. Other powders, such as the clays, require several times their own weight of water.

Obviously, thick liquid dispersions of the same consistency made by stirring whitings with water and clays with water, will have widely different solid concentrations; the whitings for example running from 55 to 70 per cent, the clays from 15 to 30 per cent by weight. A clay-water mixture of 50 per cent clay concentration or higher would be a stiff paste without any tendency to flow. It might be suitable for the potter's wheel, but not for incorporation with latex!

Besides widely varying solid content from one powder to another, these viscous liquid pastes made with pure water are very poor dispersions. They are lumpy and full of agglomerates which can be seen by spreading them on a slide and examining them microscopically, or by spinning them on a revolving glas disc and looking at the dried residue. Long continued pebble milling or repeated passage through a colloid mill will break down the agglomerates and improve the dispersion to some extent. This treatment, however, is time-consuming and unsatisfactory. There is a far quicker and more efficient method, says Van der Bilt, of reducing the thickness of pastes by using his *Darvan*, and he explains that when small quantities of this product are stirred into these thick liquid pastes, they immediately thin down to a consistency not far removed from that of pure water. The effect is instantaneous; the agglomerates are broken down and the powder particles become almost completely dispersed. A thin, smooth liquid dispersion is the result, in which intense Brownian movement may be observed under the microscope. No grinding in pebble or colloid mills is necessary, unless it is desired to further reduce the size of the ultimate particles. This, of course, may be necessary with some coarsely ground materials.

One of the principal advantages of this powerful dispersing effect of Darvan is that high concentration (50to60%) of powders may be obtained in liquid dispersed state which, without the Darvan, would in many cases be stiff, immobile pastes. Furthermore, it is possible to make from a large variety of different materials concentrated dispersions all of the same solid content.

In order to demonstrate the strong dispersion action of Darvan, a variety of different powders were individually stirred with sufficient water to give thick liquid dispersions of practically the same relative viscosity. The viscosity was measured by timing with a stop-watch the flow of 25 cc. of each dispersion from a simple apparatus designed for that purpose. Each dispersion was made so that it would have a viscosity or flownumber as close to 60 seconds as possible.

After the initial viscosity of each dispersion had been measured, a small quantity of dry powdered Darvan equal to 2% on the weight of the powder to be dispersed was stirred into the thick liquid. On dissolving, the Darvan immediately thinned down the dispersion, the new viscosity of which after a minute's standing, was then measured.

The following table gives the ratios of powder to water required to form dispersions of approximately the same initial viscosity, the initial viscosity readings, and the readings after the addition of Darvan. The viscosity measurements were all made at 24 to 25° C. The mixtures were all made in the laboratory by hand-stirring, the water being added gradually to the powder until the desired viscosity of 60 seconds was reached.

Thinning Effect of Darvan on Thick Liquid Dispersions in the proportion of 2% of Darvan on the powder to be dispersed.

MATERIAL	Mixture. Powder. grams.	Water. cc.	Viscosity (Initial) Seconds.	Viscosity with Darvan. Seconds.
Dixie Clay	10	37.0	63	3.5
McNamee Clay	10	23.2	61.5	3.5
Bentonite Clay	10	219.0	59	9
Imperial Kaolin	10	25.8	60	5
Kaolin SK	10	21.5	60	4.25
Colloid Kaolin	10	55.2	61	4.25
Osmose Edelkaolin	10	38.3	60	4
Zinc Oxide	10	17.9	58.5	4
Kadox	10	33.0	63	5
Lithopone	10	11.6	62.5	4.75
Blanc Fixe	10	11.4	62.5	4.25
Sulphur	10	12.6	58	7
Rayox	10	29.0	61	8.5
Gilder's Whiting	10	6.6	61	6
By-Product Whiting	10	8.1	60	19.25
Limestone Whiting	10	4.5	59	9
Carbon Black	10	30.8	59	10.25
P 33	10	22.9	60	8
Thermax	10	10.2	58	6
Pure Water	-	-	3	3

Now let us consider the following datas, which have been extracted from a report received from the Farben Industries Laboratories, in 1934, which will help those interested in the Latex Industry, still only in its infancy.

No single stabiliser, they say, can be obtained which is equally good as a wetting, dispersing, stabilising and thickening agent, and it would now appear undesirable if all these properties were combined in one and the same material. In certain cases especially thickening effects are by no means required. Dip mixes for instance, must generally be of thin fluid viscosity, and good suspension of the ingredients in these mixes can to a large extent be obtained by thorough dispersion. In many cases good resistance to coagulation caused by mechanical influence is required.

After very thorough and critical observation, the conclusion was reached that a stabilising agent, to be of general application in latex mixes, should be primarily a good dispersing agent and a good anti-coagulant against mechanical influences, and in addition should be capable of wetting the ingredients. For thickening, a special product was required as also for heat stabilisation. At the present stage, it is also essential, in textile impregnation, to have a special wetting agent, as the most suitable stabilisers for the dispersing of fillers only possess a moderate wetting power for textiles.

It is clearly necessary that all latex auxiliary products should satisfy the conditions of not affecting vulcanisation, ageing, colour, transperency and odour of the vulcanisates.

During the examination of the stabilisers for their dispersion and anti-coagulation properties in loaded mixes, it was found that even these two properties are to a certain extent incompatible in one and the same product. Generally speaking the coagulation resistance of latex mixes decreases as the dispersion of the ingredients is improved. A good dispersing agent for zinc oxide active or gas black yields more susceptible zinc oxide active or gas black latex dispersions, if the other conditions remain constant. The explanation of this undesirable connection is simple: the better the ingredient is dispersed, the greater is the active surface tending to coagulation.

Bearing the above facts in mind, and as the result of a very thorough series of comparative tests with many dispersing and stabilising agents, the Farben Industries Laboratories have produced their *Vultamol* which is said to combine to the greatest extent the dispersing powers and resistance to coagulation by mechanical influences. The excellent dispersive power of Vultamol for gas black in comparison with that of water and of casein solutions has been demonstrated successfully.

Vultamol also disperses zinc oxide active in a very efficient manner.

The thin liquid conistency of Vultamol dispersions is closely bound up with the good dispersion which can be obtained with this product. A dispersion of black or zinc oxide or kaolin in a Vultamol solution is distinctly more liquid than a corresponding dispersion of the same materials in water. By reason of this fact, when Vultamol is used to disperse the compounding ingredients, smaller amounts of water are required, and the solid content of the mix can be maintained at a higher level. Such mixes are characterised by a more rapid drying time, corresponding to their lower water content. The thin liquid dispersions can be mixed into the latex more rapidly and more safely, that is to say, without any fear of coagulation, and in this way the use of Vultamol should appreciably facilitate and simplify latex processing.

It is admitted that Vultamol has no effect on the cure of the mixes or on the ageing properties of the vulcanisates. In pure latex mixes, the addition of quantities in excess of 2 % causes a slight discoloration. Such large quantities of Vultamol, however, do not really come into use for unloaded mixes. The wetting power for most compounding ingredients is satisfactory, but it does not suffice for the impregnation of textiles.

The relatively low wetting power of Vultamol in comparison with materials which are essentially wetting agents is a consequence of the greater surface tension possessed by Vultamol solutions. For this reason, such solutions and the dispersion of compounding ingredients in the said solutions show no tendency to froth and the air bubbles which can be noticed during the dispersing process burst, as soon as they reach the surface. The air bubbles rise to the surface quickly on account of the low viscosity of the Vultamol dispersion. Furthermore, Vultamol does not reduce the surface tension of latex and latex compounds, so that there is no fear of the frothing tendency being increased in latex compounds which contain that material, nor are any air bubbles which may be present likely to be trapped. Tests have shown that the action of the wetting agent, which is necessary to ensure good impregnation with latex, is not influenced by Vultamol.

In addition, this product has the valuable property of delaying to a very considerable extent the increase in viscosity which occurs as a consequence of prevulcanisation or setting-up, and in contrast to casein and other organic substances, it does not give rise to putrefaction and mould formation in the latex, nor does it stabilise against the effect of heat. Latex stabilised with it against mechanical influences coagulates on heating almost as quickly as unstabilised latex or as latex to which the corresponding quantity of water has been added. No doubt this property of Vultamol is of great interest as heat sensitivity in latex compounds is very often required.

The Farben Industry give the following suggestions which are intended to serve as a guide for the use of their product: Vultamol is best applied in the form of a 10% aqueous solution. The compounding ingredients after wetting with the Vultamol solution are ground in a ball mill and the dispersion mixed into the latex. In preparing uncompounded mixes, about 5 parts of a 10% Vultamol solution is required on 100 parts of dry rubber substance, that is, on the quantities of sulphur, zinc oxide and accelerator necessary to vulcanise 100 parts of dry rubber substance, which on the average lie between the limits of 0.5 to 1.0% accelerator, 1.0 to 3.0% sulphur, and 0.8 to 2.0% zinc oxide. For compounded mixes, about 2 to 5% Vutamol should be used, that is to say 20 to 50% of a 10% solution on the total weight of the compounding ingredients. Active fillers necessitate the larger quantity being used, whilst for inactive fillers, the lower amount suffices. The minimum quantity is best ascertained by factory tests. Depending upon the type and the quantity of the filler, different amounts of water are required for pasting. It is best to use only distilled water or very soft water for latex mixes, but *water without any trace of copper in any case.* The following table gives suggestions for the approximate quantities of Vultamol solution and water:

165.0	Jatex or 130.0 Revertex
2.0	Sulphur Colloid* in lumps with 15% water
2.0	Zinc Oxide special
1.0	Vulkazit P Extra N
50.0	Filler
-	Vultamol—10% solution, see below
-	Water, see below.

FILLER.	Jatex. Vultamol Sol.	Jatex. Water.	Revertex. Vultamol Sol.	Revertex. Water.
Barytes	5.0	7.5	5.0	7.5
Whiting	7.5	12.5	5.0	12.5
Clay, Geisenhein	7.5	25.0	5.0	25.0
Clay, Seok	32.5	30.0	25.0	27.5
Dixie Clay	17.5	40.0	5.0	47.0
French Chalk	7.5	35.0	5.0	35.0
Kieselgur 19	7.5	92.5	5.0	90.0
Lithopone	7.5	7.5	5.0	7.5
Titanium White extra T	7.5	20.0	5.0	20.0

If ingredients are to be used which are not satisfactorily wetted by Vultamol, it is advisable to replace a part of the Vultamol by a wetting agent such as Igepon T, but not more than 5% of the Vultamol should be so replaced.

Before proceeding further, it is desirable to say here a few words concerning the *Ball Mill*, which is after all a very simple item, consisting of a horizontally fitted cylindrical procelain container rotating

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***Sulphur Colloid* is a gelatinous mass containing sulphur together with many other ingredients, for which purpose sulphur sublimate is most suitable. Sulphur Colloid should not be confused with *Colloidal Sulphur*, the latter being the *pure* sulphur with no admixtures in a colloidal state of distribution, and having particle sizes between 0.0001 and 0.000001 cm.

at a given speed by means of a fast and loose pulley. But the speed must be so arranged as to create no centrifugal force inside the container, which would cause the charge to stick to the walls instead of being ground. The Ball Mill is to be half filled with porcelain balls of not more than 1 inch in diameter, and the paste to be ground should only just cover the charge.

In their Report R-22 5/40, page 4, the Imperial Chemical Industries Limited suggest in the following table the optimum speed of grinding for mills covering a range of sizes as follows:

Internal diameter of the Ball Mill container in inches.	Suggested optimum speed of grinding in revolutions per minute.
4	93
6	76
8	66
10	59
12	53
15	48
18	44
21	41
24	38

From the above table, it can be seen that large mills should rotate more slowly than small ones.

Free tumbling of the grinding charge in the mill is an absolute necessity, as otherwise there would be no grinding of the material at all.

The lid for closing the container should be in porcelain and work just as the cover of a manhole in a steam boiler. To ensure perfect tightening of the lid, a rubber washer should be inserted between the edges of the lid and the opening in the container. The lid must be fitted tightly "because changes in atmospheric temperature or the warming of the charge by milling may cause the air in the container to expand and develop a slight pressure" (Report R-22 5/40, page 6, of the Imperial Chemical Industries Ltd.)

The grinding time differs from one material to another.

Zinc Oxide. We have found that a medium particle size behaved better in the ball mill and that after dispersion there is no difference in zinc oxides in so far as latex accelerator activator is concerned. It is also suggested that a low water absorption zinc oxide is desirable. Colloid Zinc Oxide must be made up of the following formula:

Zinc Oxide	....	100	parts
Gum acacia or arabic		1	„
Water	....	99	„

This should be run in the ball mill for 16 to 24 hours.

Sulphur is by far the most difficult colloid to grind, and a dispersion is prepared by various methods using protective colloids, such us glue, gums, casein etc. The formula we have used is as follows.

Sulphur	....	100	parts
Casein	....	2	„
Ammonia	....	1	„
Gelatine or Glue		1	„
Water	....	96	„

This is run in the ball mill for 30 to 36 hours.

Colours in fine powder form as are offered now-a-days are easily dispersed.

Colour	....	100	parts
Casein	....	4	„
Ammonia	....	2	„
Water	....	294	„

This should run in the ball mill for 16 hours. Colours as per the above formula, for the manufacture of balloons, should run in the ball mill for from 48 to 72 hours.

As a rule colour for latex should be insoluble in water, alcohol and acetone, and should resist also alkalis. Colours that are soluble in acetone and alcohol will not be satisfactory for balloons, gloves and the like, where a coagulant will become discoloured and can then be used only for one or possibly two colours.

Now reverting to Vultamol, it is said to have no thickening effect on latex. Its good dispersive powers for solid materials generally suffice to prevent settling altogether, or to give only a slight degree of sedimentation. Should it be found, however, in cases where very dilute latex mixes or high gravity ingredients are used, that the degree of dispersion is not sufficient to prevent sedimentation or should it be required to thicken a mix for any other reason, a special thickening agent is called for, and the Farben Industry Laboratories recommend their *Latekoll* as the most efficient active stabilizer or thickener.

Equal quantities of such active stabiliser or thickener added to a standard latex increased the viscosity in the following proportion (measured with the viscosimeter.):

Triethanolamine	1
Vultamol	1
Nekal AEM	2
Casein	2
Glue	3
Gelatine	4
Bentonite	5
Agar Agar	28

Pectin	....	260
Latekoll	....	1000

The great advantage of Latekoll over substances such as gelatine, glue, casein, pectin can be seen from this table.

Though it is always best to adjust the viscosity by previous small-scale tests, the following is intended to show the effect of Latekoll in varying concentrations in simple mixes. The viscosity varies not only with the individual supplies of latex, but also according to the various ingredients, .such as auxiliaries, fillers, vulcanising agents, the influence of which cannot be standardised completely. The viscosity of latex mixes can be seen from the wall-thickness of the dipped goods, as the wall-thickness increases with the viscosity and concentration of the latex and also depends on the speed of dipping and the type of former used.

The wall thickness of latex films is almost directly proportionate to the Latekoll concentration in the aqueous phase. The increase in the wall thickness is considerable, particularly in latex mixes with a higher rubber content, from which it can be seen that even with small additions of the thickening agent a considerable increase in thinckness of film can be obtained. The thickening of dip mixes by means of thickening agents is limited to a certain extent, however, on account of the undesirable properties which certain of these thickened latex mixes exhibit i. e. trapping of small air bubbles. Furthermore, it must be borne in mind that thicker latex films in certain circumstances take longer to dry than would a film of the same thickness built up by two separate dips. For these reasons, it is always necessary to try out new latex mixes on a small scale prior to putting them into Works operation. Such a procedure is only really necessary and of importance if mixes are to be changed or new raw material supplies are to be substituted in the Works. As far as the Latekoll itself is concerned, it is absolutely essential to conform, as closely as possible, to the methods of working which we suggest.

Like all substances which exercise a thickening action on latex, Latekoll can cause creaming in latex which contains less than 50 to 60% rubber. The creaming is influenced up to a certain point by the composition of the mix; to a great degree, however, it is dependent upon the concentration of the Latekoll itself. For example, in 35% latex, stabilised with ammonia, an addition of about 0.35% Latekoll (reckoned on the latex) is most effective. By suitably compounding the mix the creaming is diminished to a large extent. By a short and careful daily stirring, the mix can be kept homogeneous. If it is desired to avoid creaming entirely, a 60% latex concentrate should be used.

As Latekoll, like all other thickening agents, affects the dispersion if it is ground with Vultamol and the other ingredients, it *should only be added to the latex mix subsequently.* For a slight amount of thickening, sufficient to prevent sedimentation in dip mixes etc. 0.2 to 1% of the thickening agent on the water content of the mix suffices. To obtain a greater degree of thickening, such as might be required for spread mixes, either compounded or uncompounded, 3 to 5% on the water content of the mix is added. Care should be taken to ensure that the thickening agent is perfectly dispersed in the latex by thorough stirring. In order to make certain of this point, it is best to add about five to ten times the quantity of the latex mix to the Latekoll and to homegenise this thoroughly and stir in gradually the rest of the latex mix. It is important to note that the whole mix should be thoroughly homogenised.

Many specialists are convinced that perfect impregnation of a fabric with latex is only rendered possible and the processing much simplified by making use of a wetting agent. In spite of this, neither Vultamol which is used in preparing the latex mix, nor the Latekoll which is also often applied, possesses any marked wetting powers for textiles.

The number of wetting agents suggested for latex impregnation of fabrics is great. Many wetting agents were tested, both in respect of their wetting power in conjunction with latex, and from the point of view of their satisfactory behaviour in latex mixes and in the vulcanisates. The result of this thorough examination is, says the Farben Industries Laboratories, that their product called *Igepon T Powder Highly Concentrated*, is the most suitable wetting agent for the impregnation of fabrics with latex mixes.

Igepon T Powder Highly Concentrated can be used with advantage by making a 10% solution which is added to the latex mix after the incorporation of the other ingredients. The addition of 1 to 2% Igepon T Powder Highly Concentrated, reckoned on the water content of the mix, generally suffices. After thorough tests, it was found that this addition of Igepon T facilitates the penetration of the latex mix into the fabric and considerably improves the adhesion of the rubber film to the fabric and the adhesion between the individual fabric plies.

It is suggested that still better adhesion can be obtained by previously impregnating the fabric with Igepon T solution which has the effect of rendering it more absorptive. It is still said to be necessary to incorporate the Igepon T in the latex mix.

This is the method put forward by the Farben Industries Laboratories. The Imperial Chemical Industries, in their suggestions for rubberising fabrics, propose another method, which we shall discuss in the following chapter, when discussing the method tried by the author and adopted by him for some years now with very satisfactory results.

In conclusion, it may be stated that for *preserving latex* and to avoid putrefaction and mould formation, the Farben Industries Laboratories recommend two other products:

Preventol Liquid N, and
Preventol Liquid I.

Preventol Liquid N is used in quantities of 0.1 to 0.2%, and Preventol Liquid I in quantities of 0.05 to 0.1%, reckoned on the latex. They say that the best method of incorporation is to dilute the Preventol with water 1 to 1 before adding it to the latex.

As an anti-coagulant, ammonia at medical strength of .882 was generally used in the various plantations, where the author has studied latex on the spot.

Potassium Cyanide has been found effective as an anti-coagulant when 2% of a 2% solution was used. To prevent premature coagulation Sodium Bisulphite is used also in the proportion of 1 to 2 oz. of a 10% solution in 5 gallons of latex.

CHAPTER II.

Accelerators, Anti-oxidants, Fillers and Oils used in Latex.

ACCELERATORS. Almost all the Vulkazits used for ordinary rubber mixes can be used in latex mixes also. Both the water-soluble and the water-insoluble Vulkazits may be used. But the *water-soluble* accelerators cannot be used in all processes, particularly where a separation of the serum takes place, on depositation on porous moulds for instance, whereas the *water-insoluble* accelerators can be applied more generally, and their application presents no difficulties, as they can be made into a paste-form like other solid materials, such as sulphur and zinc oxide, and incorporated in the latex as a fine dispersion.

It is obvious that the choice of an accelerator depends primarily upon the conditions of processing and cure of the finished articles, also on the purpose of the mix. But it is necessary to differentiate between very active accelerators which cure even at room temperature like the Vulkazits P and 774 and those which only bring about cure at higher temperatures. So when rapid cures at comparatively low temperatures are desired, the *Vulkazits P, 774 and P extra N* should be used, whereas, if it is desired to produce mixes, which show no traces of pre-vulcanisation during the different stages of manufacture or during long periods of storage and which will cure in a longer time at higher temperatures, then the less active accelerator such as *Mercapto* and *Thiuram* are to be preferred.

(a) *Vulkazit P*—an ultra-accelerator—is a water-soluble crystalline product, yellowish-white in colour, possessing a weak amine-like odour. The following quantities will dissolve in 1000 ccs. of water:—at 20° C about 50 grams, at 80° C about 330 grams.

In preparing the latex mix, Vulkazit P is ground separately from the other ingredients with some Vultamol solution and then added to the latex. This accelerator should not be ground with the other ingredients, as difficulties may easily occur due to bad dispersion. The good solubility of Vulkazit P in benzol also makes it possible to produce a solution with the accelerator, into which thin unvulcanised articles, which contain no accelerator are dipped for their vulcanisation.

Articles made with Vulcazit P Vulcanise at room temperature in a few days. By increasing the temperature, the time of cure can be reduced accordingly. By using 0.6% Vulkazit P and 2% sulphur colloid in lumps with 15% water calculated on the dry rubber, the following cures can be obtained in hot air, at

110° C. in about 15 to 20 minutes, or
100° C. in about 30 to 40 minutes.

(b) *Vulkazit 774* is also water-soluble, although in lesser degree than Vulkazit P.

In 1000 ccs. of water its solubility is:
at 20° C. about 5 grams, and
at 80° C. about 10 grams.

As for the incorporation of this accelerator in latex mix, the same instructions apply as in the case of Vulkazit P.

The relatively limited solubility of Vulkazit 774 in water may be considered an advantage in case the cure of dipped goods is to be carried out in hot water.

Dipped articles from latex mixes containing 0.36% Vulkazit 774 and 1.1% of sulphur colloid in lumps with 15% water, calculated on the dry rubber content, cure in about 15 minutes in water at 90° C.

For hot air cures, the conditions are the same for Vulkazit 774 as for Vulkazit P.

Quick cures at low temperatures can be obtained with the combination of these two ultra-accelerators. The vulcanisation of articles containing 0.3% Vulkazit P and 0.3% Vulkazit 774 in hot air takes place as follows:

10 to 15 minutes at 110° C. or
about 30 minutes at 90° C., or
40 to 50 minutes at 80° C.

(c) *Vulkazit P extra N* is a water-insoluble accelerator, tasteless and odourless.

A special advantage of this accelerator is illustrated by the behaviour during storage of mixes in which it is incorporated, no tendency to setting up or viscosity alteration being noticeable. The fact that this accelerator is insoluble in water enables articles to be cured satisfactorily in hot water. The curing times, using 1% Vulkazit P extra N and 2% sulphur colloid in lumps with 15% water, calculated on the dry rubber substance, are:

in hot air	15 to 20 minutes at 110° C.
	30 to 40 minutes at 100° C.
	60 to 80 minutes at 90° C.
	3 to 4 hours at 70° C.
	15 to 18 hours at 50° C.
In water	30 minutes at 85° C.
	15 minutes at 95° C.

Vulkazit P extra N is the most suitable accelerator for use in the manufacture of all odourless and tasteless rubber goods. In preparing the mixes, Vulkazit P extra N is made into a paste with the other ingredients and so added to the latex.

The less active accelerators, such as:

(a) *The Vulkazit Thiuram* is practically insoluble in water. This accelerator with the other compounds is made into a paste and incorporated in the latex. Latex mixes with Vulkazit Thiuram possess relatively good storage properties. The curing time of mixes containing 0.3% Vulkazit Thiuram and 2% sulphur colloid in lumps with 15% water calculated on the dry rubber substance is, in hot air 30 to 40 minutes at 115° C. and 15 to 20 minutes at 125° C.

Latex mixes with a higher content of Vulkazit Thiuram say 2.0 to 3.0% on the dry rubber substance can also be vulcanised without sulphur. Such mixes are of particular interest for heat-resisting goods and for stocks which come into contact with bare metals like silver, mercury and copper, as owing to the absence of free sulphur, discoloration of the metal is to large extent avoided. The curing time in such cases is 45 to 60 minutes at 125° C. in hot air.

(b) *Vulkazit CT* is a water-soluble, viscous accelerator, which is heated at about 40° C. in water prior to incorporation into latex. This accelerator is of special interest for *ebonite goods.* The mixes should be made without zinc oxide, as when this ingredient is present, longer cures are required.

(c) *Vulkazit Mercapto* is a water-insoluble accelerator which can be incorporated into the latex without any difficulty, if it is made into a paste with the other ingredients, using the Vultamol solution. If other less powerful stabilising agents are used, Vulkazit Mercapto easily gives rise to coagulation of the latex mix on incorporation. Vulkazit Mercapto can cause also thixotropy in latex mixes containing zinc oxide.

Neither latex mixes with Vulkazit Mercapto nor the articles made from such mixes vulcanise at room temperature, and higher temperatures are necessary to bring about satisfactory cures.

(d) *Vulkazit DM* is also practically insoluble in water. It is made into a paste with the other solid ingredients of the mix by using a Vultamol solution, and then stirred into the latex. Vulkazit DM mixes cure more slowly than Vulkazit Mercapto mixes and thus longer curing times or higher curing temperatures are necessary. Latex mixes with Vulkazit DM show much less tendency to thixotropy than those in which Vulkazit Mercapto is used. Vulkazits Mercapto and DM are chiefly used for articles requiring longer cures at higher temperatures. Neither of these accelerators cause any discoloration during the cure.

By adding stearic acid or zinc stearate to Vulkazits DM and Mercapto mixes much better tensiles and higher modulus figures can be obtained from the vulcanised goods.

Below are brief descriptions of accelerators recommended by the Monsanto Laboratories as suitable for latex work.

Their *RN 2*, which is a new ultra-accelerator, is not only suitable for milling into rubber on ordinary mixing rolls, but for latex stocks as well. It is an accelerator capable of giving fast cures at low temperatures, particularly in hot air, whereas there have been only one or at the most two accelerators, produced on the market, which even approached the speed of cure required and both these materials suffered from the disadvantage of causing the compounded latex to thicken. RN 2 can be used for all these applications with the added advantage that the total acceleration cost is quite low. Naturally, where the thickness of the article to be cured is great, one cannot expect a very fast cure, as to-date there is no practical method of speeding up the transfer of heat from air to rubber.

Our tests with RN 2 have definitely established that the said accelerator provides for faster cures than any other material commercially available. Most latex work can be carried out with a basic formula as follows:

Latex as 60% dry rubber	100^{k} 000
Zinc Oxide	1^{k} 000
Sulphur ...	1^{k} 500

An addition of 1.25% of RN 2 to this stock allows for a good cure being reached in 5 to 20 minutes at 158° F. and in 2 to 10 minutes at 180° F., whilst in water at 100° C. a tensile strength of well over 5000 lbs. per sq. inch is obtained in 3 minutes.

Even good cures have been obtained with the sulphur proportion as low as 0.25% with slightly higher amounts of RN2, but it is our experience that it is not necessary to use such very low sulphur content to obtain good ageing, for instance 1.5% RN2 with 0.75% sulphur gives equally good ageing with a lower accelerator cost. Such stocks will cure in hot air at 122° F. in 30 to 60 minutes. In general, 1% or 1.25% RN 2 with 1% sulphur is quite sufficient for most applications, and it is only when the best possible ageing is required that one should increase the RN2 to 1.75% by dropping the sulphur proportionately.

Being a liquid, RN 2 is very easily dispersed, the standard formula for it being:

RN 2	100 parts.
Oleic Acid	5 ,,
Ammonia	2 ,,
Water	93 ,,

The oleic acid should be added to the RN2 stirring thoroughly, then the ammonia, stirring again, and finally water. For this purpose there is no need to use a mechanical stirrer, as a glass rod or spatula will do the work satisfactorily. But care should be taken that not too much ammonia is added, as otherwise emulsification will be retarded and additional water required. Similarly, if the ammonia or water is added to RN 2 before the oleic acid, crystallisation will occur, and this will show up in the form of brown spots in the film.

It is nevertheless important to add the RN 2 as an emulsion, otherwise, if the RN 2 is simply washed in with water, full activation is not obtained and the films may show spots where the RN 2 has agglomerated.

Channel Blacks exert a definite retarding effect on RN 2 even when the black concentration is only 5%. A soft black such as Castex, however, appears quite satisfactory in concentration up to 10% on the dry rubber.

Another material causing retardation of cure is *Carbon Tetrachloride.* This retardation by chlorinated solvents such as Carbon Tetrachloride, Ethylene Dichloride etc. appears common to several accelerators. But if benzol or naphtha is used, no difficulty will be experienced and normal cures will be obtained. As usual, where benzol is used alone as a solvent, the cure is slightly quicker.

For transparent articles RN 2 is a very suitable accelerator. Being rubber soluble, it dissolves in the rubber and provided the latex is properly compounded with low zinc oxide and low sulphur contents, good transparent articles are obtained in hot air or water. Several manufacturers have been using water-soluble accelerators. Whilst a few of these give good transparency, they are all liable to decomposition owing to slow hydrolysis with subsequent loss of strength. For the best transparency, combined with low acceleration cost, RN 2 is excellent.

It may be remarked that RN 2 is not always supplied in a liquid form, but often as crystals. These crystals are dissolved 50:50 in heated pure paraffin oil, and then the accelerator is ready for use.

The amounts of RN 2 shown in the formulas apply to the liquid accelerator.

Pipsolene and R 23. Where a slower rate of cure is desirable, equivalent results to those obtainable with RN 2, but in a longer time or at a higher temperature, are obtainable with Pipsolene. This accelerator is also rubber-soluble and in regular production is used for transparent articles such as dipped goods and for self-vulcanising cements. The speed of cure is much slower and in general is not fast enough for present day curing technique, when temperatures much below 200° F. are employed. The same good ageing properties are apparent as with RN 2, and Pipsolene gives excellent transparency. The use of either of the two accelerators is recommended for obtaining the best transparency equal to that obtained with powdered insoluble accelerators.

Pipsolene is dispersed as follows:

Pipsolene	....	100	parts
Ammonia	....	2	„
Water	....	98	„

Ammonia should be added to Pipsolene and well stirred, then water, stirring again with a glass rod. These emulsions are so easy to prepare that it is generally unnecessary to store them.

Certain materials can be used with Pipsolene to speed its rate of cure. One such product is *R 23*, an aqueous solution, which when used in 0 5 or 1.0%

concentration on dry rubber in conjunction with Pipsolene, activates the latter and gives faster cures at temperatures down to 180° F. But for Curing *below* this temperature, RN 2 should be used alone. Being an aqueous solution R 23 needs no special emulsification. It should be added slowly, preferably diluted with an equal volume of water, direct to the latex.

Pip-Pip is chemically Piperidine Pentamethylene Dithiocarbamate and is available under such trade names as P. P. D., Vulkazit P, Accelerator 552 and perhaps others. This product is a water-soluble powder. Whilst considerable use has been made of Pip-Pip in the past, it is now being largely replaced by other more stable materials, owing to its water solubility and subsequent tendency to hydrolysis.

For the dispersion of Pip-Pip, dissolve it in 10 to 20 times its weight of water at 150 to 180° F. A 5% solution of Pip-Pip may be prepared for use, and tests indicate that this solution—in distilled water—is satisfactory even after 5 months. It may be remarked that 5% is the limit of solubility for Pip-Pip where temperature falls to 50 or even 40° F.

The Ultra Zinc DMC is chemically Zinc Dimethyl Dithiocarbamate also known as Zimate. Other derivatives are also available on the market such as the Diethyl and Butyl compounds as well as various ethyl-cyclo-hexyl and certain other metallic salts with cadmium. Most of these salts of dithiocarbamic acid are interchangeable, and whilst possessing reasonable activity, appear to be one of those capable of replacement by the RN 2 type accelerator with both a reduction in cost and an increase in efficiency. Many are water-insoluble powders and as such need grinding in a ball mill before dispersion. The dispersion of ultra Zinc DMC is done as follows:

Ultra Zinc DMC	100	parts
Casein	6	„
Ammonia	2	„
Water	92	„

and should run in the Ball Mill for 6 to 8 hours.

R2 Crystals is an ultra-accelerator and is the reaction product of carbon bisulphide with methylene dipiperidine. It is used for curing liquid latex cements. This accelerator is readily emulsified and like RN2 crystals is soluble in latex. At low temperatures around 220° F. it gives approximately the same rate of cure as RN2.

A-1 which is a Thiocarbanilide, was one of the first organic accelerators known to the industry. It was widely used for a number of years, but has gradually been replaced by the newer accelerators. Today A-1 may be considered as a special-purpose accelerator. It is used to some extent in tyre bead stocks and footwear. It is used to advantage in conjunction with R-2 crystals and RN 2 crystals to obtain exceedingly fast cures at low temperatures. These combinations of accelerators are finding favour in quick-curing naphtha cements and rubber latex.

Slower Speed Accelerators. For some purpose it is impracticable to use fast-curing ultra-accelerators, since in a composite article, one part becomes over-cured before the remainder commences curing. Unfortunately, most semi-ultra-accelerators such as acidic thiazoles and derivatives therefrom cause bad thickening and coagulation of the latex. There are one or two materials which can be safely used, and more will be developed. One of the few that have been found very satisfactory is *A-32.* This accelerator is on the market under various trade names such as Butene, 808, B. A., and is of the same nature as Vulkazit 576.

The use of *A-32* imparts very good ageing qualities and the accelerator is only slightly retarded by Carbon Black. Being a liquid, it is very easily dispersed and is to be preferred when it is desired to produce a latex having no tendency to thicken on storage and when curing is to be carried out at temperatures around 260 to 270° F.

A-32 is dispersed as follows:

A-32	....	100	parts.
Oleic Acid	....	5	,,
Ammonia	...	2	,,
Water	....	93	,,

B. *Anti-Oxidants.* In general, the ageing properties of rubber goods made from latex are very good, provided the mixes are correctly composed and the time and temperature of cure are accurate. This is no reason why anti-oxidants should not be added to rubber stocks. In fact their action is to delay the perishing of the rubber compounds until a considerably longer period has elapsed than would normally be the case.

There are many anti-oxidants. The Imperial Chemical Industries recommend their *Nonox* of which much good can be said, whereas the Farben Industries Laboratories recommend their *Aldolalphanaphthylamine*, their *Phenylalpha* and *Phenylbetanaphthylamine* and their non-staining *Anti-oxidant MB*, all water-insoluble materials which are to be made into a paste in the Ball Mill with the other powders before being added to the latex.

Up to now no such product as a *Non-staining Anti-Oxidant* has been produced, and all of us have learnt that any effective anti-oxidant discolours white rubber compounds to a certain extent and that this discoloration is very pronounced when the stock is exposed to bright sunlight or to ultra-violet light. The Monsanto Chemicals agree that their Flectol H and Flectol B are not exceptions to this rule, but what they affirm is that their Flectols are the least staining of the present day effective anti-oxidants, and it is said that they provide the maximum oxidation resistance in latex work, the use of both Flectols giving excellent results.

The Monsanto *PNB* is sometimes used in latex compounds as an anti-oxidant, although, since the oxidation resistance of the naphthylamine type is generally considered to be less than that of the Flectols, the latter are generally preferred. The Flectols should be dispersed by the following methods:

A.	Flectol B	....	100	parts.
	Oleic Acid	....	5	„
	Ammonia	....	2	„
	Water	....	93	„
B.	Flectol H	....	100	parts.
	Casein	....	4	„
	Ammonia	....	2	„
	Water	....	94	„

Both the above are to be run in the ball mill for about 24 hours, after which the dispersion will be perfect.

Anti-oxidants, as we have just said, have no protective action against cracks caused by atmospheric influence called *Sun cracks.* The Farben Industries Laboratories have composed an anti-oxidant called *Ramasit WD Concentrated* which they say is very effective against the formation of such cracks. Being a paraffin emulsion, it is a thin liquid at about 30° C and can be easily incorporated into the latex in which it should be added after all the fillers have been incorporated. The quantities to be used vary between 5 to 10 parts to 100 parts of the dry rubber substance.

When larger quantities are used, Ramasit WD Concentrated also acts as a softener in which case its use will give to the finished product smooth non-tacky surfaces.

Ramasit WD Concentrated is recommended also in the case of single texture proofing on very thin fabric on which the penetration of the latex mix is often noticed. To avoid this, it is suggested that the fabric should be previously impregnated with a dilute 1% solution of Ramasit WD Concentrated. But it is admitted that the adhesion of such impregnation to the fabric is rather reduced and is generally not found to be quite sufficient.

As already stated in Chapter I of this part, there is another method of obtaining a perfect adhesion of the latex impregnation to the fabric which the author intends to develop in the next chapter.

C. *Oils.* These should be emulsified before being incorporated in latex mixes, but there is no single formula which will emulsify all oils. We have found that most mineral oils are emulsified easily by the following methods:

1.	Oil	....	70	parts.
	Oleic Acid	....	15	,,
	Triethanolamine		5	,,
	Water	....	10	,,
2.	Cycline Oil	....	100	parts.
	Oleic Acid	....	15	,,
	Triethanolamine		3	,,
	Water	....	80	,,

The oleic acid should be added, to the oil and mixed thoroughly, whereas the triethanolamine should be stirred in the water. Then the oil-oleic acid is added to the latter and mixed *slowly* while stirring.

As regards Cycline Oil, when it is used in quantities above 5% on the rubber content, it will soften the latter notwithstanding the fact that this softening is not as evident as in milled rubber. Another point of importance is that large quantities of oil will cause blooming and give a greasy tacky surface to the finished product.

3. Materials having a higher degree of viscosity such as the Monsanto Accelerator A-16 must be treated as follows:

A-16	100 parts.
Casein	7 „
Ammonia	2 „
Santomerse	1 „
Water	90 „

The temperature of this mix should be kept at about 120 to 180° F. until all materials are dissolved and the mix should be stirred continually while cooling.

4. Other materials emulsify more readily by using 5 parts of oleic acid, 2 parts of ammonia and 93 parts of water.

In some cases, it is necessary to use a combination of all four of the above said methods.

D. *Fillers.* The main fillers for latex mixes are the *Barytes*, *Blanc Fixe*, *Whiting*, *Kaolin*, *and Silicious Chalk*. *Gas Blacks* are generally used to impart a black colour to the mixes.

The influence of the various fillers on the properties of goods produced from latex mixes corresponds to the effect of these fillers in ordinary rubber mixes. For instance, different grades of the same filler can yield goods of different qualities. This is often the case with Kaolin. So, when using different qualities of the same filler in latex mixes, attention should be paid to the different behaviours on pasting, incorporation into latex and into the unvulcanised latex mixes. The Farben Industries Laboratories, in their report, already referred to, a good deal of which appears in this part of the book on latex, give the following details with some of the principal points of interest in the prepartion of latex compounds:

Barytes and Blanc Fixe both have fairly high specific gravity and they easily tend to cause sedimentation in the mixes. The use of small quantities of *Latekoll* with these fillers is therefore advisable.

Whiting together with *Kaolin* is probably the most widely used filler in latex mixes. Depending on the quality of the Whiting used, the colour of the goods varies from yellowish to a greyish shade. The various types of Whiting differ widely in regard to the necessary quantities of Vultamol-Solution and water which have to be used to bring about good dispersion and to avoid coagulation.

Latex concentrated 60%	165^k 000
Sulphur Colloid in lumps with 15% water	2^k 000
Colloid Zinc Oxide	5^k 000
Titanium Dioxide	5^k 000
Vulkazit P	0^k 300
Vulkazit 774	0^k 300
Whiting (see below)	50^k 000
Vultamol—10% solution (see below)	-
Water (see below)	-

To reduce the ingredients of the above mix to a paste, it is suggested that the following quantities of Vultamol-Solution and water should be taken when different types of Whiting are used.

Whiting.	*Vultamol-Solution*	*+ Water*
"Suprema"	7	7
"Burka F"	25	8
"Lipsig Precipitated"	40	65

As these figures show, the amounts of Vultamol and water necessary to paste the fillers satisfactorily and to avoid coagulation must always be determined by preliminary tests.

Kaolin. Similar variations on pasting occur when different types of this filler are used. The following data is intended to be of interest to latex manufacturers:

Latex concentrated 60%	165^{k} 000
Sulphur Colloid in lumps with 15% water	2^{k} 000
Colloid Zinc Oxide	2^{k} 000
Vulkazit P	0^{k} 500
Vuklazit 774	0^{k} 500
Kaolin (see below)	50^{k} 000
Vultamol (10% solution—see below)	-
Water (see below)	-

Kaolin Geisenheim	10.0	Vultamol-Solution	+ 25	water
Dixie Clay	15.0	,, ,,	+ 35	,,
Stockalite	12.5	,, ,,	+ 35	,,
Devolite	10.0	,, ,,	+ 30	,,
Rubber Clay H	10.0	,, ,,	+ 25	,,

Apart from the varying behaviour on pasting, the different grades of Kaolin also influence the viscosity of the latex mixes to a varying extent. In the above series of tests it was found that *Dixie Clay* gave the maximum increase in viscosity and the effect was rather less with *Rubber Clay H.* Much less thickening was noticed in the case of *Stockalite* whilst both *Kaolin Geisenheim* and *Devolite* gave practically no thickening at all. This thickening action of some Kaolin can be made use of in manufacturing proofed fabrics. Mixes of this type are especially suitable for the first coat on the fabric, if the ordinary latex mix does not give a sufficiently smooth surface.

The hardness and elasticity of the goods are also influenced to a marked extent by the choice of the filler. As is generally known, Kaolin gives considerably harder goods than do the Whiting or Barytes. However, even the various kinds of Kaolin give different degrees of hardness. On examining vulcanisates containing different sorts of Kaolin, those with Rubber Clay H were found to have the greatest hardness, followed by Dixie Clay, Stockalite and Devolite, whilst Kaolin Geisenheim gave the least hardness, but the greatest elasticity. The colour of the goods is also influenced by the different types of Kaolin.

Carbon Black is mostly used in latex mixes as a colouring agent. It can easily give rise to coagulation when incorporated into it.

The use of Vultamol as a stabiliser and dispersing agent has, however, given very good results in this connection. After numerous tests, it has been found best with a view to obtaining uniform dispersion, to take a small amount of Carbon Black and paste it separately with a Vultamol solution. Only when satisfactory dispersion in the medium is obtained are the other ingredients to be added to the paste together with the remaining quantity of Vultamol-Solution and water. The whole is then homogenised until a completely uniform paste is obtained. When attempts were made to paste the Carbon Black with other fillers, it was found that a much inferior degree of dispersion was obtained.

Zinc Oxide is necessary in almost all mixes as an activator for the accelerator. To facilitate its incorporation in the latex mixes, the product should be ground and reduced to a paste in the Ball Mill so as to obtain as small particles as possible and a better dispersion, whereby less sedimentation takes place. Such Zinc Oxide as those called by the Farben Industries Laboratories *Zinc Oxide Special* or *Zinc Oxide Active* is the colloid zinc oxide of which we have already spoken.

Lithopone or *Titanium Dioxide* and *Titanium White Grades* are *White Pigments* which can be used in latex mixes, provided they are made into a paste in the Ball Mill.

Stearic Acid. In many mixes, principally those which contain Vulkazit Mercapto or Vulkazit DM, an addition of stearic acid is advantageous as this material brings about a considerable improvement in the tensile properties and yields snappier vulcanisates. *But it has been found that instead of stearic acid, it is advisable to use Zinc Stearate in latex mixes as it is easier to incorporate it, although it gives practically the same results as stearic acid.*

The incorporation of Zinc Stearate is best obtained by mixing it with an ammoniacal-Vultamol-solution in order to have a paste consistency and then to stir it into the latex to which the other ingredients have already been added. To reduce the Zinc Stearate to a paste, it is best to use 10 parts of a 10% Vultamol-Solution into which 2½ parts of ammonia have been added. By this method perfect dispersion of the Zinc Stearate can be obtained in the minimum time.

Various grades of *Factices*, specially prepared for incorporation in latex compounds, are now being used. These have also the advantage of being easily emulsified.

Their addition to mixes for proofed fabrics yields a softer and smoother surface. For this purpose the Factice should be reduced to a paste by the addition of an ammoniacal agent, after which it can be added to the latex compound.

Finally, with regard to *Sulphur*, a fine dispersion of this product is essential to obtain a good uniform cure of the articles. Its sedimentation in the latex mixes is prevented by the use of the finest possible grade of that product. It has already been explained in what way sulphur should be ground in the Ball Mill so as to obtain that colloid product which is an absolute necessity in any latex compound.

Rubberol Perfumes. The suitability of these for use with latex mixes has already been referred to in Part I, Chapter VI. They are pasted up with the fillers, using a Vultamol-Solution and the required quantity of water. The paste is first mixed with about ¼ or ⅓ of its volume of latex and then stirred into the bulk of the latex until the whole has become a homogeneous mass. The quantity of Rubberol Perfumes to be incorporated into the latex compound depends chiefly upon the method of vulcanisation adopted and the degree of perfume desired. For hot air cures, a higher amount of Rubberol should, however, be used.

From this brief information about the different fillers, it will be appreciated that, depending upon the type of fillers and the processing conditions, the properties of the mixes and consequently of the articles can be altered within very wide limits. It is therefore essential to satisfy oneself about each filler for the purpose in view by carrying out the necessary tests. For this purpose it is hoped that the information given above will serve as a useful guide.

CHAPTER III.

Latex Mixes and Latex Fabrication.

AS already stated in the previous chapter, for the preparation of latex mixes, the different ingredients for incorporation into the mix should be made into a paste beforehand with a *protective colloid and dispersing agent*, using 1% of the product, calculated on the dry rubber in the latex, in the case of *Aresklene* or *Santomerse*, and a 10% solution of the material in the case of *Vultamol*. These products generally are called *Wetting Agents*, and they can also act as *stabilisers*. It may be noted that some wetting agents, used in the textile trade, are very effective, when freshly mixed in the latex, but due to their acidity they make the latex unstable, and in case of overdose they will coagulate it in less than 24 hours.

The lowering of the surface tension in water is not an indication of a similar decrease in surface tension in latex, nor does a low surface tension in latex signify fast wetting. There are several wetting agents which reduce the surface tension of latex to 30, while an equal concentration of *Aresklene* will give a surface tension of 32 to 33 and a faster wetting.

The Monsanto *Aresklene* and *Santomerse* are first class wetting agents and are very effective when present in 1% concentration on the dry rubber content. They have also the property of stabilising the latex, when only a lesser quantity, say from 0.10 to 0.25% is used.

Wetting agents and stabilisers increase the foaming tendency of the latex and help to lengthen the period of drying. When used in high concentration, they make the dried film hygroscopic with a soapy, greasy feel.

In order to obtain a fine paste of uniform consistency, the necessary quantity of water should be added to the wetting agents, and the whole mass thoroughly ground in the porcelain Ball Mill. The auxiliary effect of a mechanical grinding apparatus such as a Ball Mill is necessary in spite of the helpful properties of a good dispersing agent. Even though the particles of the material it is wished to disperse may be very small, either as the result of previous grinding or through the type of precipitation process, they generally adhere together so closely-that they cannot be separated without mechanical aid. In other cases the particles are so big that it is first necessary to grind them specially. A good dispersing agent helps the grinding effect enormously, and what is of greater importance is that it prevents subsequent agglomeration. In order to obtain maximum results from a very efficient grinding process, the use of good dispersing agents is essential. The incorporation of dry fillers in the latex or the addition of latex to the dry powder *must always be avoided*, as this will give rise to insufficient wetting and completely unsatisfactory dispersion of the fillers in addition to readily causing coagulation. Some ingredients like the Monsanto special products, RN2 Crystals, RN2, R2 Crystals, Pip-Pip, or products from other makers such as Vulkazit P and 774, Ramasit W. D. Concentrated, Latekoll or Igepon T are stirred into the latex separately from the other ingredients. Gas Black and the dyes are also pasted separately.

To paste the compounding ingredients, either 1% of Aresklene or 5% of a 10% Vultamol solution, reckoned on the dry rubber in the latex will prove satisfactory in the case of unloaded mixes, whilst generally 20 to 50% of the 10% Vultamol-Solution or 1% of Aresklene on the total of the compounding ingredients will suffice in loaded stocks.

In incorporating small amounts of fillers, it is best to mix them after they have been pasted with two or three times as much latex and then to stir the mixture obtained into the remaining bulk of the latex. In this manner a rapid and uniform dispersion of the ingredients in the latex will be obtained. In making heavily loaded mixes, gradual addition of the pasted fillers to the latex is advisable. After all the fillers have been added, the mixes should be thoroughly homogenised. Care must be taken that the blades of the stirrer do not rub against the sides of the container, as this may cause partial coagulation. In many cases it is desirable to add a *thickening agent* to the latex mixes, either to prevent settling of the fillers or to raise the viscosity of the mixes. For this purpose *Latekoll* is very suitable. It is only added *after* the fillers and the vulcanising agents have been incorporated into the latex. About 0.2 to 1.0% of Latekoll reckoned on the water content of the mix is sufficient to prevent settling of the compounding ingredients. If a greater degree of thickening is required, 3 to 5% of *Latekoll* should be used.

As materials for containers for latex mixes, cypress wood, enamelled sheets, porcelain and well-tinned sheet iron soldered inside, are recommended. Iron, zinc and aluminium containers *should not be used.* As already explained, in order to avoid all possibility of copper poisoning, apparatus made of copper or brass *should never be used for latex work* in any circumstance.

As for the Rubberising Machine for porducing proofed goods with latex, we suggest that the knife should be made of cypress wood or of tinned steel, the latex compound being spread upon the fabric from a wooden container placed in front of the machine just above the knife.

The cure of latex mixes takes place in the usual way, depending upon the type of article. Thus it can be in hot air, in room temperature, wrapped on the drum, in the press, in open steam or in hot water.

Rubberised Fabrics. In cases, says Farben Industry Laboratories, where latex mixes are used for impregnating textiles, an addition of Igepon T Powder Highly Concentrated is necessary, and *the greater the degree of wetting, the better is the impregnation and the adhesion between the plies.* Still better adhesion, they say, can be obtained by previously impregnating the fabric with an Igepon T solution, which has the effect of rendering it more absorptive. Igepon T Powder Highly Concentrated is best added to the latex mixes at the end in the form of a 10% aqueous solution using 1 to 2% of that product on the water content of the mix.

On the other hand, the Imperial Chemical Industries Ltd. in their suggestions as to how to rubberise fabrics with latex compounds recommend that the fabric, before being coated with the latex mix, should be impregnated with one of their water-solution products, such as Waxol W, Waxol PA or Velan PF, and that the impregnation should be followed by ironing the cloth to prevent the latex mix from percolating through the fabric in the course of fabrication.

Both the above methods do not give the results one would expect, for the following two reasons:

1. By impregnating the fabric with the water-solution and then ironing it before proofing with the

latex compound, much time is lost, thereby reducing the output capacity of the factory.

2. By pasting the fabric as suggested both by the Imperial Chemical Industries and Farben Industry Laboratories, the rubber coating cannot adhere perfectly to the cloth and often the so doubled proofed fabric can be separated and the inner rubber layer detached completely from the cloth to which it is intended to adhere firmly.

A method of making the latex compound adhere firmly to the fabric is by partially coagulating the said compound with metal salts, so that the charge on the latex particles is reversed, thereby increasing its viscosity.

The latex compound so applied adheres to the negatively charged fibres with the result that it will be well bound into the fabric. Royce J. Noble suggests that instead of reversing the charge on the latex particles, the fabric should be dipped in a positively charged colloid, such as an aluminium-hydroxide-solution, prior to coating it with the latex compound, as in this case the negatively charged latex particles form a strong bond to the positively charged fabric (Latex in Industry page 219). More can be said regarding this electro process. Cockerell in 1903 patented a method for coagulating latex electrically. His object was to separate the negatively charged particles in the latex and fix them on an electrolytic cell so that the particles so deposited on the anode were to form a layer of rubber on its surface, producing therefrom a sticky coagulum, the particles of which, as long as the coagulum was wet, could be removed by reversing the electrical charge. For reversing the charge on the particles, it has already been stated that some metal salts should be added to the stabilised latex until the hydrogen-ion-concentration of the latex is somewhat below pH7. The said particles then become positively charged and, under the influence of the electrical current, deposit themselves on the cathode.

This is the principle adopted in the electro-plating process, and can as well be applied in the case of rubber, so that articles made of metals, such as wire screens and the like can be protected with rubber against any corrosive action. Interesting information regarding this electro deposition can be found in "Latex in Industry," pages 271 to 277.

We now expose here the method which the author has definitely adopted, after two years of successful trials, for coating fabrics with latex compounds:

A first coating of a thin layer of rubber mix dissolved in a solvent should be applied to the fabric. For a reason which will be explained later such coating *must* penetrate the structure of the cloth. Then when the solvent has evaporated, the rubberising of the fabric may be continued with the latex compound by applying as many latex coatings as may be required. In the case of doubled fabrics, care should be taken that both the proofed cloths pass between the well tightened and heated rollers of the Doubling Device, when the latex compound is still more or less wet and tacky. By this process, the fabrics will adhere firmly to each other after vulcanisation.

As latex compounds were having indisputable advantages such as low cost of production and elimination of costly solvents, when they were first introduced into practical factory work a few years ago, all of us were convinced that from that time onwards no more rubber dissolved in solvents would be used in the fabrication. This was only an assumption, which up to now has not fully materialised, and soon we realised that by using latex no similar good results could be obtained to those achieved by using rubber solutions.

The reason is that the latex is an aqueous colloid which cannot wet the textile fibres, usually coated with starch and oils for their dressing purpose.

We would state again that particles of rubber in the latex are quite different from the swollen rubber compound dissolved in the solvent. Furthermore, when coating the fabric with a rubber solution, the solvent attacks the fibre of the texture, dissolves the greasy materials composing the dressing, and penetrates the fibre of the fabric with the rubber it has dissolved.

On the contrary, the water content of the latex is incapable of wetting the textile fibre, and it also cannot dissolve the greasy materials of its dressing.

Now, as Royce J. Noble remarks, the rubber particles in a non-swollen condition are charged electrically, and when the rubber particles in the latex come into contact with the electrically charged individual fibres of the fibrous material, they are repulsed and sometimes coagulated, with the result that, even if the rubber particle penetrates the structure of the fabric, it cannot go very deep into it. We do not mean that by having a stabilised latex with a noticeable reduced surface tension, the textile fibres may not be more or less wetted facilitating thereby the superficial coating of the fabric, but it will never be equal to the result one can expect by coating the cloth with a thin layer of rubber solution before proofing the fabric with the latex compound. Furthermore, as an additional precaution, to render the impregnation of the fabric more easy, it may be boiled as explained in Chapter II of this part of the publication, which will free the texture from oils, greases and starch.

At the time of writing this book, there is a very large demand for *Groundsheets.* The double rubberised fabric consists of muslin and sheeting. These have to be coated with a rubber compound composed of rubber, sulphur and mineral matter such as zinc oxide and other fillers. Accelerators should be added to the mix to improve the rubber compound and to help vulcanisation. The proofing is to be free of grit from copper and manganese and their components and also from lead chromate. The said proofing should not contain more than 0.5% of iron, or iron components, calculated as $Fe_2 O_3$. It must also not contain reclaimed rubber, must not have more than 5% of organic matter extractable by acetone and not more than 5% of organic matter extractable by alcholic potash after removal of the material extractable by acetone. These percentages are to be calculated on the weight of the rubber in the compound.

The weight of the groundsheet is stipulated generally to be at so many ounces per square yard.

Some specifications also state that the groundsheet should be *hot vulcanised.* What we understand from this, is that the proofing should not be vulcanised with sulphur chloride, which operation is called the *cold cure.* In our opinion the implication of the term *hot vulcanisation* is not very clear. It might mean that the fabric, well protected, should be vulcanised in steam, at say round about 300° F., or that it should be cured in *hot air,* in a double jacketted vulcaniser, at 212° F., or in the tropical room temperature, at about 80° F, which may also be called hot air.

In any case for the preservation of the textile fibre, we would recommend to vulcanise the rubberised cloth at as low a temperature as possible, and we suggest that the best is the room temperature. The mix should contain:

Rubber	....	55%
Sulphur not more than		3%
Fillers	....	42%

and a small addition of any accelerator to improve the rubber compound and to assist its cure. We have adopted the Monsanto RN2, which has proved most successful, and we have divided the weight of the mix into two equal parts, as follows:

A. 50% of the weight of rubber and fillers plus the sulphur.

B. 50% of the weight of rubber and fillers plus the Accelerator RN 2.

Compounds A and B, made with raw rubber, are dissolved in a solvent for the first coating to be applied on to the fabrics; and for the subsequent coatings A and B are composed with latex.

Mixes A and B, kept separately, can stand safely for months, but as soon as they join together, vulcanisation starts, which completes in hot air at 212° F., in a few minutes, and at room temperature in a few days.

The fabrics are coated preferably on the DOUBLE RUBBERISING MACHINE, first with solution A applied say on the muslin, and with solution B applied on the sheeting. Both the knives of the machine should be sufficiently raised to allow a thin layer of the rubber solution to impregnate both the fabrics.

Then, when the solvent has evaporated, the fabrics can be coated with the latex mixes A and B, the compound A being composed of half the quantity of latex and fillers, plus the sulphur, the compound B of half the quantity of latex and fillers, plus the Accelerator RN 2.

For coating with latex, the knives of the Double Rubberising Machine as already said, should be of cypress wood, to prevent premature coagulation of the mix. The knives should be sufficiently lifted to allow the formation of a layer of rubber compound thick enough to obtain the specified weight per square yard.

Coating of latex compounds on fabrics to be doubled can be done either by dry or wet method.

The dry method is simple and needs no explanation, as when the coatings on the fabric are thoroughly dry, they are doubled between the tight rollers of the Doubling Device and then vulcanised.

The wet method is employed when a large production of rubberised fabric is desired. But with this process the water-proofing of the fabric is poorer than that obtained when the dry method is adopted. The adhering properties of the fabric are, however, noteworthy in this case.

For the wet method, both the compounds A and B already mentioned, should be thickened as much as possible. The thickening can be done by the addition to the compound of locust bean gum or any glue. When the compounds are applied to the fabrics at a thickness regulated by the tension exercised on the cloth and by the given angle of the spreading knives, the rubberising machine should run as fast as possible, the fabrics then joined between the doubling device being wound up tight on the take-off roll, on which they will remain until completely dry.

In the following pages are a few formulas for producing various items. These formulas have been composed with the products suggested by the Farben

Industry Laboratories. The quantities shown in these formulas are reckoned on the weight of 100 parts of dry rubber substance in the latex, corresponding to about

130 parts by weight of a 75% latex concentrate, or
165 ,, ,, ,, 60% ,, ,, ,, or
250 ,, ,, ,, 40% ,, ,, ,,

In the case of Igepon T and Latekoll, they are calculated on the water content and used as suggested on pages 352 & 353. In the formulas, therefore, the quantity of Igepon T is left blank, as this will depend on the water content of the type of latex used and the amount of water subsequently added to the mix.

The quantities of sulphur in the following mixes refer to *colloid sulphur in lumps with 15% water*, and thus the true sulphur content of the mix is 15% less. If sulphur in paste form, containing 70% sulphur is used, the quantity of colloid sulphur indicated in the formula should be increased by about 20%.

Vultamol is to be used as a 10% aqueous solution.

For proofed fabrics the Farben Industries Laboratories recommend their Vulkazit P, 774 and P extra N.

Hereafter is a typical formula, as suggested by the Farben Industries Laboratories, for rubberising fabrics:—

			ccs.
No. 1.	Dry Rubber substance	10^{k} 000	
2.	Sulphur Colloid (15% water)	0^{k} 200	
3.	Vulkazit P	0^{k} 050	
4.	Vulkazit 774	0^{k} 050	
5.	Ramasit W. D. Conc.	1^{k} 000	
6.	Black P. 33	0^{k} 500	
7.	Whiting	8^{k} 000	
8.	Colloid Zinc Oxide	0^{k} 300	
9.	Distilled Water		2000

		ccs.
10.	10% Vultamol-Solution. Take 20 to 50% of it on the total weight of the compounding ingredients.	-
11.	Latekoll 1% on the water content	190
12.	Igepon T (10% aqueous solution) 1 to 2% on the water content.	1900

The method for preparing the above mix is as follows:

(a) Nos. 2, 3, 4 and 5 are to be pasted up with 250 ccs. of the 10% Vultamol solution well pasted in the ball mill by adding 500 ccs. of distilled water and then stirred into 5000 ccs. of latex (the equivalent of a gallon is 4.5435 litres, equal to 4543.5 ccs.).

(b) No. 6 (500 grams of P33) is made into a paste in the ball mill with 250 ccs. of the 10% Vultamol solution.

(c) Nos. 7 and 8 are made into a paste with 1000 ccs. of the 10% Vultamol solution.

(d) Now add Nos. 7 and 8 to No. 6 in the ball mill and produce a rubber liquid paste by mixing it with 1500 ccs. of distilled water. Then stir in the remaining 5000 ccs. of latex

(e) Stir (a) into (d).

(f) Finally, add to the compound 190 ccs. of Latekoll and 1900 ccs. of a 10% Igepon T solution and stir thoroughly to form a homogenous paste.

Remark: 20 grams of Carbon Black P 33 can be dispersed with 80 ccs. of distilled water plus 10 ccs. of a 10% Vultamol-Solution.

The cure of the above mentioned mix can be effected as follows:

about 10 to 15 minutes at 110° C.
or 30 „ at 90° C.
or 40 to 50 „ at 80° C.

Latex mixes which contain the ultra-accelerators Vulkazit P and 774, in addition to sulphur and zinc oxide, cure in room temperature after 3 to 4 days. The processing of these mixes is not affected by any prevulcanisation.

Proofed fabrics generally require special treatment of the surface to improve the appearance and the feel. Depending upon the desired effect, the proofings can be powdered with maize, talc or mica dust, or they can be varnished.

For varnishing, *Acronal L 100* which is an aqueous emulsion mixable in all proportions with latex is specially suitable. The latex-proofed fabrics are coated once or twice with a latex-Acronal mixture of approximately 300 to 500 parts by weight of Acronal L 100 and 100 to 200 parts by weight of the latex mix used. After drying, the fabric is cured in the usual way. By this treatment with the Acronal-latex mix, the feel and gloss of the proofing is considerably improved and the water absorption and tendency to light cracking notably reduced.

Proofing for Jute:

Dry Rubber Substance	100^k 000
Sulphur Colloid	2^k 000
Whiting	50^k to 100^k 000
Zinc Oxide Colloid	3^k 000
Igepon T Solution	-
Ramasit WD Conc.	5^k to 10^k 000
Vulkazit P	0^k 400
Vulkazit 774	0^k 400
Phenylbetanaphthylamine	0^k 800
Vultamol-Solution	10^k 000
Distilled Water	10^k to 15^k 000

Cure in hot air: 10 to 15 minutes at 110° C.

Proofing Stocks with Vulkazit P extra N:

(a)	Dry Rubber Substance	100^{k} 000
	Sulphur Colloid	2^{k} 000
	Colloid Zinc Oxide	2^{k} 000
	Vulkazit P extra N	1^{k} 000
	Whiting	80^{k} 000
	Ramasit WD Conc.	5^{k} to 8^{k} 000
	Titanium Dioxide	2^{k} 000
	Vulcanosol Blue GG	4^{k} 000
	Vultamol-Solution	20^{k} 000
	Distilled Water	25^{k} 000
	Kaolin	20^{k} 000

Cure in hot air: 30 minutes at 110° C.

(b)	Dry Rubber Substance	100^{k} 000
	Sulphur Colloid	2^{k} 000
	Colloid Zinc Oxide	3^{k} 000
	Vulkazit P extra N	1^{k} 000
	Kaolin	80^{k} 000
	Gas Black P 33	5^{k} 000
	Ramasit WD Conc.	10^{k} 000
	Aldolalphanaphthylamine	0^{k} 400
	Vultamol-Solution	50^{k} 000
	Distilled water	50^{k} 000

Cure in hot air: 30 minutes at 110° C.

Rubberised Fabrics with Vulkazit Thiuram:

Dry Rubber Substance	100^{k} 000
Colloid Zinc Oxide	5^{k} 000
Vulkazit Thiuram	0^{k} 300
Sulphur Colloid	2^{k} 000
Vultamol-Solution	5^{k} 000
Distilled Water	5^{k} 000

Cure in hot air: 30 minutes at 115° C., or 20 minutes at 125° C.

Vulkazit Thiuram Mix without Sulphur:

This latex mix is recommended for *Shoe fabrics* containing bare metals such as copper and brass wires.

Dry Rubber Substance ...	100^{k} 000
Colloid Zinc Oxide	5^{k} 000
Vulkazit Thiuram	from 3^{k} to 3^{k} 500
Antioxidant MB	0^{k} 500
Vultamol-Solution	5^{k} 000
Distilled Water	5^{k} 000

Cure in hot air: 40 to 50 minutes at 125° C.

Compounds with Vulkazit Mercapto or Vulkazit DM:

Dry Rubber Substance	100^{k} 000
Sulphur Colloid	2^{k} 500
Colloid Zinc Oxide	5^{k} 000
Vulkazit Mercapto or DM	0^{k} 500
Zinc Stearate	1^{k} 500
Vultamol-Solution	15^{k} 000
Ammonia (specific gravity 0.910)	0^{k} 600

Cure in the press: 15 to 20 minutes at 138° C.

Cure in hot air:

for Vulkazit Mercapto:

50 to 60 minutes at 110° C., or
30 to 35 „ 125° C., or
10 to 15 „ 141° C.

for Vulkazit DM:

80 to 90 minutes at 125° C., or
25 to 30 minutes at 141° C.

Remark: To paste the Zinc Stearate, 4 parts of the Vultamol-solution plus 0.6 parts ammonia are used. The remainder of the Vultamol-solution is used to paste the other compounding ingredients.

Mixes with Vulkazit TR plus Vulkazit Mercapto have proved very useful for stocks for *driving belts*, when ammonia stabilised latex concentrates are used, the fabric being Duck No. 1000 having a warp of 12/14 and weft of 12/8.

Dry Rubber Substance	100^{k} 000
Colloid Zinc Oxide	10^{k} 000
Sulphur Colloid	1^{k} 750
Phenylbetanaphthylamine	1^{k} 000
TR-Mercapto combination (see Remark below).	0^{k} 800
Igepon T solution	....
Whiting	20^{k} 000
Vultamol-Solution	10^{k} 000
Distilled Water (if required)	

Cure in the press: 20 minutes at 138° C.

Remark: The combination of Vulkazit TR and Vulkazit Mercapto is as follows:

20 parts by weight of Vulkazit Mercapto are dissolved in 80 parts by weight of Vulkazit TR with slight heating.

Dipped Goods. Christopher Columbus must have seen not only rubber balls in Haiti, when he landed for the first time on American soil, but perhaps many other articles made of rubber in a rudimentary way. Shoes, for instance, as we gather now, must have been in vogue there for centuries, as they are there still in vogue today.

The Natives produce these shoes in a peculiar way. Instead of shaping them by means of moulds, as we do, they used to dip their own feet in the latex and then, as in the case of the Amazon Para, allow the latex to coagulate by keeping the feet over the smoke produced by fire-wood.

Those of us who were interested in the rubber industry before the Great War must have come across shoes of this kind. They were called "Savates" on the European rubber markets, where they were much appreciated on account of their "para" quality.

Hundreds of years later, following the example set by the American pioneers, we ourselves started the manufacture of dipped rubber goods—first from rubber solution and later on from latex—as we have now come to realise that the advantages of producing seamless goods from latex are numerous. First the quality of the rubber is improved, as it does not lose its ageing properties and conserves its natural nerve; whereas, with rubber dissolved in a solvent, not only is the solvent costly, but the rubber, owing to the mastication process for making it into a good solution, loses its molecular aggregation and oxidises quickly. Further, it gets partially destroyed by the cold vulcanisation process, which, in early days, was the only method of vulcanisation employed.

Manufacture of goods from latex is not always an easy task, and one has to check principally the degree of the viscosity of the compound, which can give rise to many troubles. If it is excessive, air bubbles are produced in the walls of the dipped goods, and if it is too low, the compounding ingredients may easily separate, when producing goods of a thin film.

The latex mix has therefore to be compounded with much care, and if proper precaution is taken when mixing the various ingredients in the latex, most of the troubles can be obviated. When the mix is ready and poured into the tank for use, it should be allowed to stand for at least 24 hours, so that the air contained in the compound may rise to the surface and escape. Care should be taken to see that the tank remains tightly closed during these 24 hours with a wet cloth on the cover so that any air which penetrates may be charged with humidity. If a skin formation is detected on the following day, it should be carefully skimmed off.

Dipped goods are now-a-days produced by means of a "Dipping Apparatus". We have designed a very simple one, which consists of a glass-lined tank of 4′ x 4′ x 2′, inside which is a platform capable of being moved upwards and downwards, kept in position by means of a chain attached to a hand-wheel. A rack with the forms attached is suspended below the platform. The forms are immersed into the latex as quickly as possible, say in 10 to 15 seconds, and withdrawn in 2 to 6 minutes according to the size of the forms. Care should be taken that the withdrawing operation is done without shocks and at a uniform speed till the top of the form emerges from the surface of the latex compound, when drops, if any, are allowed to drip off. A plate should be kept under the form to prevent any drops falling again into the latex, which may cause the formation of air bubbles.

The rack is then completely lifted and detached from the platform to be inverted for drying the film. When completely dry, subsequent dips may be made, but the forms should not be immersed as deep as with the first dip.

Tanks other than glass-lined, are in use for latex work. Those made of cypress wood are very good, provided they have their inside walls coated with an alkali-resisting paint. Tanks can also be made from metal, but no galvanised or zinc sheets should be used for the well known reason that zinc is bound to react with the ammonia in the latex. For the same reason aluminium is also to be avoided. Black iron can as well be used for latex dipping-tanks, provided they are painted inside with a rust-proof solution.

The forms used for dipping are usually made of glazed or unglazed porcelain. Goods produced with glazed porcelain are transparent, whereas those with unglazed porcelain forms are dull and opaque. Unglazed porcelain forms are required when a coagulant is applied on the forms to obtain in one dip a thicker film of latex.

Forms can also be made of glass and wood. In the latter case, they should be polished and preferably lacquered with the following mixture:

50 parts of celluloid dissolved in 50 parts of acetone or acetate d'amyle.

The application of a coagulant to the forms before dipping them into the latex is now generally adopted, as it saves time, a film of 1 mm. thick being produced with a single dip. This is ideal if there are no pin-holes appearing on the dipped material, in which case a second dipping is required. "Latex in Industry", page 252 and 253 gives a few interesting formulas for the coagulants to be applied to the forms in different cases:

For Household Gloves:

Alcohol	....	85
Formic Acid	....	15
Perfumes	....	as desired.

For Balloons:

Alcohol	....	60
Formic Acid	....	16
Ammonium Acetate		12
Water	....	12

For Surgical Gloves:

Alcohol	95
Tannic Acid	5

The following is a good coagulant formula, but it has the disadvantage of having a water absorption tendency.

Calcium Chloride	30
Acetic Acid	2
Water	70

Remark: When using any of the above coagulants, the ammonia content of the latex should be reduced by 0.1 to 0.2%.

Another method of producing seamless goods in a rapid manner is to vulcanise them partially by dipping the dried dipped articles in a solution of 10 grams Vulkazit P plus 10 grams Vulkazit 774 dissolved in 1000 ccs. of Benzol. When this solution has evaporated, further dippings can be made, the forms being immersed after each fresh dip in the benzol-vulkazit-solution. After this the goods can be cured in hot air as will be explained in the following pages.

For dipped goods an addition of a small quantity of Latekoll in the latex compound—suggests the Farben Industry Laboratories—has the effect of preventing the settling of the compounding ingredients, and 0.2 to 1.0% of this product reckoned on the water content of the mix, will be found sufficient.

Mixes for Prophylactics:

(a)	Dry Rubber Substance	100^{k} 000
	Sulphur Colloid	1^{k} 100
	Colloid Zinc Oxide	0^{k} 600
	Vulkazit 774	0^{k} 360
	Vultamol-Solution	5^{k} 000
	Latekoll (as stated in previous pages)	....

Cure: in water: 15 minutes at 90° C.

(b)

Dry Rubber Substance	100^{k} 000
Sulphur Colloid	1^{k} 800
Colloid Zinc Oxide	0^{k} 500
Vulkazit P extra N	0^{k} 600
Vultamol-Solution	2^{k} 500
Latekoll	....

Cure in hot air: 30 minutes at 110° C.

Mix for Observatory and Toy Balloons:

Dry Rubber Substance	100^{k} 000
Sulphur Colloid	1^{k} 500
Colloid Zinc Oxide	0^{k} 600
Vulkazit P extra N	1^{k} 000
Vultamol-Solution	3^{k} 500
Latekoll	....

Cure in water: 30 to 35 minutes at 95° C.
in hot air: 60 to 70 minutes at 110° C.

It has already been remarked that some American balloons have inside the mouth piece an *unvulcanised rubber layer* which makes it possible to close the balloon by pressing the mouth piece. This layer of rubber which contains neither accelerator nor sulphur, is painted inside the mouth piece after the balloon has been cured.

Some balloons are *printed with pictures.* The printing of designs on ballons is done with a rubber solution containing a fairly large amount of pigment colours. The balloon must be slightly inflated and the solution must either be sprayed thinly with the help of stencils or be printed from a stamping pad.

The following mix is useful:

Pale Crepe well masticated	100	parts.
Titandioxide	50	„
Vulcan colour Powder	50 to 100	„
White Gloria Factice	100	„

The mix must swell in white spirit and must further be diluted with white spirit, the quantity depending on whether the printing is done by means of a stamping pad or by spraying.

Red Teat Mixes:

(a)	Dry Rubber Substitute	100^{k} 000
	Sulphur Colloid	2^{k} 000
	Colloid Zinc Oxide	2^{k} 500
	Vulkazit P extra N	1^{k} 000
	Cadmium Red BB	2^{k} 000
	Vultamol-Solution	6^{k} 000
	Latekoll	....

Cure in hot air after thorough drying at room temperature: 20 minutes at 110° C.

(b)	Dry Rubber Substance	100^{k} 000
	Sulphur Colloid	2^{k} 000
	Colloid Zinc Oxide	2^{k} 500
	Vulkazit P	0^{k} 600
	Cadmium Red B	2^{k} 000
	Vultamol-Solution	6^{k} 000
	Latekoll	....

Cure: as mentioned above for (a).

Surgical Gloves made from the following mix have excellent ageing properties and resistance to sterilisation. After ageing them for 35 hours in water in an autoclave at 120° C., it was found that the stock still had very good mechanical properties.

Latex Concentrated 60%	165^{k} 000
Sulphur Colloid	1^{k} 800
Colloid Zinc Oxide	0^{k} 800
Vulkazit P extra N	0^{k} 600

Vultamol-Solution	2^{k} 500
Latekoll	....
Revertex-Mineral Oil 1:1	10^{k} 000

Cure in water: 15 minutes at 95° C. or
30 minutes at 85° C.
Cure in hot air: 20 minutes at 110° C. or
60 minutes at 100° C.

In the manufacture of gloves from latex mixes, it often happens that thin spots appear between the fingers. These are caused by the latex film which forms between the fingers splitting only when the finger tips come out of the latex compound. This can be prevented by the addition to the mix of a mineral oil emulsified with Revertex. With such mixes the film breaks much earlier, and a uniform thickness is obtained.

Household Gloves:

(a)

Dry Rubber Substance	100^{k} 000
Sulphur Colloid	2^{k} 000
Colloid Zinc Oxide	2^{k} 000
Vulkazit P extra N	1^{k} 000
Whiting	30^{k} 000
Titanium Dioxide	5^{k} 000
Cadmium Red GG	0^{k} 330
Vultamol-Solution	9^{k} 000
Distilled Water	9^{k} 000
Revertex-Mineral Oil 1:1	6^{k} to 10^{k} 000
Latekoll	....

Cure in water: 30 minutes at 95° C.

(b)

Dry Rubber Substance	100^{k} 000
Sulphur Colloid	2^{k} 000
Colloid Zinc Oxide	0^{k} 600
Vultamol-Solution	5^{k} 000
Latekoll	....

When dried, the articles are dipped in a solution of 10 grams Vulkazit P plus 10 grams Vulkazit 774 in 1000 ccs. of benzol, then cured in hot air for 20 minutes at 100° C.

Heated Forms can be used also for the manufacture of dipped goods with the same effect as forms coated with a coagulant. But forms for this purpose should naturally be made of metal so that they can be preheated, or continuously heated by means of inner electrified coils. Such forms are dipped in *heat-sensitised latex mixes* containing certain salts which under the influence of the heat emanating from the forms cause the latex to coagulate on to them.

To work with heated forms is of course a special branch of latex fabrication. Salts such as Ammonium Nitrate or Zinc Salts or Sulphate of Calcium or Diphenyl-guanidine, in the proportion of about 1% on the weight of the compound, are generally used for heat sensitised mixes. It is necessary after the forms have been coated with latex by this process, that they must be thoroughly washed with a view to the elimination of sensitising agents, as the latter would otherwise exercise an unfavourable influence on the ageing properties of the goods. When the washed products have been dried, they can be cured.

The Farben Industry Laboratories state that Anti-Oxidant MB also exercises a heat sensitising effect, specially in ammonia stabilised latex mixes, and the main advantage of using MB as a sensitising agent lies in the fact that even mixes containing a large proportion of fillers, say 100% of Whiting or more, can be processed without difficulty and that in this case the articles need not be washed before their cure. Furthermore, MB brings about a marked improvement in the ageing properties of the goods.

3 to 5% on the weight of the latex of the 1:1 emulsion Mineral Oil-Revertex has been proved necessary to prevent the formation of cracks which sometimes occur when drying thick coats on the forms.

The heat-sensitising effect of MB is illustrated in the following mixes, the thixotropy or viscosity of these mixes being considerably increased by the presence of this anti-oxidant.

A.	Latex Concentrate 60%	....	165^{k} 000
	Sulphur Colloid	....	2^{k} 000
	Colloid Zinc Oxide	....	1^{k} 000
	Vulkazit P extra N	....	1^{k} 000
	Vultamol-Solution	....	5^{k} 000
	Revertex-Mineral Oil	1:1	10^{k} 000
	Anti-Oxidant MB	From 0 to	0^{k} 800

After one dip of the *heated forms*, articles of the following thickness were obtained after drying and curing on the forms:

Time of Dipping	Condition of the Forms.		Thickness of the article	
	Heated	Cold	Without MB	With MB
20 seconds	70° C.	-	0.07 mm.	0.88 mm.
20 seconds	100° C.	-	0.13 mm.	1.40 mm.
20 seconds	-	Cold	0.05 mm.	0.13 mm.

The difference in the thikness of the goods containing MB when dipped with cold forms is caused by the greater thixotropy of the mix.

B. The influence of various quantities of MB on the thickness of the goods after one dip can be seen from the following:

Latex Concentrate 60%	...	165^{k} 000
Sulphur Colloid	....	2^{k} 000
Colloid Zinc Oxide	....	4^{k} 000
Vulkazit P extra N	....	1^{k} 000

Vultamol-Solution	....	5^{k} 000
Distilled Water	....	2^{k} 500
Revertex-Mineral Oil 1:1		8^{k} 000
Anti-Oxidant MB		From 0^{k} 5 to 1^{k} 200

The dipped goods were dried overnight at room temperature and then cured for 20 minutes in hot air at 110° C. The cured articles were found to be of the following thickness:

Time of Dipping	Condition of the forms.		Thickness of the Article.	
	Heated	Cold	With 0.5 MB	With 1.2 MB
10 seconds	70° C.	-	0.43 mm.	1.12 mm.
20 seconds	70° C.	-	0.59 mm.	1.36 mm.
10 seconds	100° C.	-	0.77 mm.	1.55 mm.
20 seconds	100° C.	-	1.00 mm.	1 90 mm.
20 seconds	-	Cold	0.12 mm.	0.14 mm.

C. Latex Concentrate 60%		165^{k} 000
Sulphur Colloid	....	2^{k} 000
Colloid Zinc Oxide	....	8^{k} 000
Vulkazit P extra N	....	1^{k} 000
Whiting	....	100^{k} 000
Vultamol-Solution	....	30^{k} 000
Distilled Water	....	20^{k} 000
Revertex-Mineral Oil 1:1		10^{k} 000
Anti-Oxidant MB		From 0 to 0^{k} 800

By heating the forms at 100° C., one dip of 20 seconds duration gave articles of the following thickness:

Without MB	*With MB*
0.2 mm.	0.9 mm.

D. Latex Concentrate 60%		165^{k} 000
Sulphur Colloid	....	2^{k} 000
Whiting	....	33^{k} 000
Vulkazit P extra N	....	1^{k} 000
Colloid Zinc Oxide	....	4^{k} 000

Antioxidant MB	....	0^{k} 800
Vultamol-Solution	....	4^{k} 000
Distilled Water	....	12^{k} 000
Revertex-Mineral Oil 1:1		6^{k} 000

Various moulds for producing balls were half filled with the latex mix D, and whilst being constantly rotated were heated in a water bath at 80° C. Within five minutes the mix began to set forming a ball about 3 mm. thick. The same mix but *without MB* showed no degree of setting at all under these conditions.

Then further tests were carried out in a mould with a core, the distance between the mould and the core being 3.5 mm. The mould was filled with a latex mix containing MB and heated up to 100° C. Within a few minutes the latex mix was completely set so that it could be taken out of the mould and cured after drying.

We now give below the method adopted by Van der Bilt in the preparation of a latex compound with the ingredients he supplies. Where he states in his formulas "Casein" and "Caustic Soda", it is to be understood that he is referring to solutions of these products.

For instance his Casein 15% is a mixture of:

Casein	....	15.0	grams.
28° NH_3	....	6.7	,,
Distilled hot water		78.3	,,

and his 25% Caustic Soda mixture is composed as follows:

Caustic Soda	25	grams.
Distilled hot water	75	,,

Formula A.

Latex Dry Rubber Substance		100^{k} 000
Colloid Zinc Oxide	....	2^{k} 000

Sulphur Colloid	0^k 600
Age Rite White	1^k 000
Butyl Zimate	1^k 000
Latex Telloy	0^k 500

Formula B.

Colloid Zinc Oxide	2^k 000
Sulphur Colloid	0^k 600
Age Rite White	1^k 000
Butyl Zimate	1^k 000
Latex Telloy	0^k 500
15% Casein Solution	0^k 153
25% Caustic Soda Solution	0^k 100
Darvan	0^k 204
Distilled Water	4^k 643

Formula C.

Colloid Zinc Oxide	2^k 000
Sulphur Colloid	0^k 600
Age Rite White	1^k 000
Butyl Zimate	1^k 000
Latex Telloy	0^k 500
15% Casein Solution	1^k 020
Darvan	0^k 204

The above three formulas are mixed together in the Ball Mill.

Van der Bilt has also described the manufacture of *Latex Coated Cotton Gloves.* They are rubber-coated by dipping them, on properly shaped forms, into a suitable latex mix, and they are vulcanised after being dried.

The forms are either of wood or porcelain, the dimensions being such as to completely fill the glove snugly without stretching it. The fingers of the form should have as much separation from each other as possible, and the thumb should incline forward and not sidewise with relation to the palm. The forms are usually made in two pieces, the thumb being separate and detachable. Three or four dozen forms are placed on a rack and dipped at one time.

Van der Bilt suggests that the tank containing the latex compound should have a circulating device to prevent settling, and a baffle plate at each end to prevent frothing and skin formation. The immersion of the gloves is done quickly to prevent too much penetration through the fabric, and during the draining the forms are turned backwards and forwards to ensure an even deposit.

The forms are dipped twice. After the first dip the deposit is dried for 10 to 20 minutes at 140° F. Drying of the first deposit should not be carried too far, otherwise poor adhesion of the second deposit may occur. After the second dipping and draining, the gloves are dried and cured for 20 to 30 minutes in an oven at 220° F. They are then finished by dipping in a water shellac solution and allowing to dry. The shellac treatment is used to give a high gloss and to eliminate the tacky surface of the rubber.

Rubber coated gloves are most commonly made in black, white and translucent colours. The latex formulas shown in the next pages have been developed especially for glove dipping and are giving splendid results commercially. For translucent coatings the latex is simply mixed with the vulcanising dispersion. For black or white coatings dispersions of P-33 or Rayox, in addition to the vulcanising dispersion, must be added to the mix.

The vulcanising dispersions are made by grinding the ingredients together, in the proportions shown, in a pebble mill for at least 48 hours. If frothing is encountered, caustic soda and casein should be added only during the last hour of grinding as a 15% casein solution with part of the total water. The function of casein and caustic soda is to prevent the agglomeration of the ingredients in the dispersion during storage and to increase the stability of the final latex mix.

In the case of the Rayox dispersion, which is used for colouring the latex compound for white gloves, prolonged grinding in a pebble mill is unnecessary; one or two hours being sufficient.

The P-33 dispersion, which is used for colouring the black compound, is ground overnight in a pebble mill.

The black compound may also be made by substituting the vulcanising dispersion used in the translucent compound for the one shown in the black formula; however most black glove compounds need to be acid-resisting and for this reason the dispersion containing Age Rite White is used. It may be noted here that Age Rite White increases the resistance of the rubber to the action of acids.

The coatings obtained by using these latex compounds are very strong and tough. They cure rapidly at low temperatures and resist ageing remarkably well.

To make the shellac solution, the water is heated to boiling and the borax dissolved in it. The shellac is then gradually stirred into the hot borax solution and the heating is continued until the solution becomes clear. The solution of shellac should be diluted with an equal volume of water before using.

Latex Mixes for Coating Cotton Gloves are as follows:-

A. *Translucent*

Rubber (as 60% Latex)	100^{k} 000

Vulcanising Dispersion

Colloid Zinc Oxide	1^{k} 000
Sulphur Colloid	1^{k} 000
Butyl Zimate	1^{k} 000
Darvan	0^{k} 120
15% Casein Solution	0^{k} 120
25% Caustic Soda Solution	0^{k} 100
Water distilled	2^{k} 660
Total	6^{k} 000

B. *Black.*

Rubber (as 60% Latex)	100^{k} 000

Vulcanising Dispersion.

Zinc Oxide Colloid	2^{k} 000
Colloid Sulphur	0^{k} 600
Age Rite White	1^{k} 000
Butyl Zimate	1^{k} 000
Latex Telloy	0^{k} 500
Darvan	0^{k} 204
15% Casein Solution	0^{k} 153
25% Caustic Soda Solution	0^{k} 100
Water distilled	4^{k} 643
Total	10^{k} 200

The following *Colour Dispersion* is added to the above.

P-33	5^{k} 000
Darvan	0^{k} 200
Water Distilled	3^{k} 100
Total	8^{k} 300

C. *White.*

Rubber (as 60% latex)	100^{k} 000

Vulcanising Dispersion.

Colloid Zinc Oxide	1^{k} 000
Colloid Sulphur	1^{k} 000
Butyl Zimate	1^{k} 000
Darvan	0^{k} 120
15% Casein Solution	0^{k} 120
25% Caustic Soda Solution	0^{k} 100
Water Distilled	2^{k} 660
Total	6^{k} 000

With the following *Colour Dispersion.*

Rayox	10^{k} 000
15% Casein Solution	0^{k} 300
Water distilled	9^{k} 700
Total	20^{k} 000

The gloves are finished with a Shellac solution, as follows:—

Shellac	10^{k} 000
Borax	2^{k} 500
Water	87^{k} 500
Total	100^{k} 000

Rubberising of Roads. Considerable work on the subject has been done chiefly by the Rubber Research Institute in Malaya. Years ago they made a number of experiments incorporating a small percentage of latex in various types of bitumens and pitch, but apparently without very much success. Later on, they tried to mix large quantities of fillers into latex, but again, owing to difficulties with coagulation, had little success. As a result of this experimental work, the attempt to use natural latex was given up for the use of a concentrated type of latex, which is very much more stable. The whole of the work done recently in connection with this problem, has been described in detail in the Annual Reports and Journal of the Rubber Research Institute of Malaya for 1931, 1932 and 1933.

Apparently the cheif difficulty in the earlier work was that even if they managed to get satisfactory mixing of the fillers with the latex by the use of suitable protective agents, drying of the mix caused cracking and shrinkage due to the natural contraction of the rubber.

Probably the most successful results have been obtained by the use of fillers, which act as dehydrating materials compounded with a concentrated latex. These fillers are of the nature of cements of various kinds. Coagulants having a delayed action have also been used to prevent cracking, and *Sodium Silico Fluoride* is one of these. A complete formula for a compound which has been used for surfacing roads is as follows:

Rubber (as 60% latex)	100^{k} 000
Colloid Sulphur	1^{k} 000
Zinc Oxide Colloid	3^{k} 000
Accelerator Ultra Zinc DMC	1^{k} 000
Carbon Black P-33	5^{k} 000
Sodium Silicate	8^{k} 000
Sodium Silico Fluoride	4^{k} 000
Aluminous Cement (Fire Clay)	280^{k} 000
Antioxidant Flectol H	2^{k} 500

This composition was applied over a roughened bitumen road previously covered with a thin cement layer. Since sodium silico fluoride causes rapid coagulation of the layer within a short period after application, the compound must be made up in a stirring apparatus capable of keeping the materials intimately mixed.

The latex is first put in the mixer, and then the fillers, previously prepared in the Ball Mill, added slowly and thoroughly stirred in, after which the compound is ready to be poured, and the resultant surface layer on the road dries rapidly after coagulation and may be used within three to six days. This compound has apparently given the best results so far, but the chief difficulties are still those of suitable adhesion to the underlayer, prevention of oxidation and means of satisfactory vulcanisation. The protection against oxidation has been improved by the addition of anti-oxidants such as Flectol H, but still owing to the effect of the sun some cracking will probably take place after a few months. The accelerator used is one of the Piperidine type or similar ultra-accelerator, in this case the Ultra Zinc DMC.

Other *moulded goods*, such as soles and heels, can be made from latex compounds. The method of manufacture in this case is to fill a mould with the latex mix which is then allowed to dry. The process is not so simple as one might imagine. The difficulty is to have a perfect distribution of the mix over the surface of the mould. The best way of successfully carrying out this process is to work with a gel latex obtained by the combination of metallic salts, instead of a concentrated latex. This was demonstrated by Victor Henri some thirty years ago.

In our opinion, however, at the present stage of the latex industry, such fabrications are only possible in the laboratory and cannot be exploited very easily on a factory scale.

Tubes can also be made from latex, but once again as trials in the laboratory and not in the factory, for extruding latex in the shape of a tube and coagulating it in a bath is very easy to suggest, but very difficult to realise. Then why not dip the mandrel coated with a coagulant in a bath filled with latex compound? All this seems quite possible, but how many tubes can be produced in a day by such a process?

Artificial velvet, and *Suede* can also be made from latex, but these fabrications have not yet reached the stage when they can be brought into actual production in the factory.

Latex Paper and *Artificial Leather*, however, can be produced now-a-days in the factory. Many patents describe the methods for combining the latex with the material suitable for producing paper, and this fabrication has been described by Royce J. Noble in *Latex in Industry*, pages 280 et seq.

Rubber Goods for the Foodstuff Industry, such as *Bottle Rings* and *Bottle Stoppers* can also be made from latex but only in the laboratory. For those who wish to try the above-said fabrications, we give below a few formulas for producing such articles:

	A.	B.
Latex Dry Rubber Substance	100^{k} 000	100^{k} 000
Colloid Sulphur	2^{k} 000	2^{k} 000
Colloid Zinc Oxide	2^{k} 000	2^{k} 000
Vulkazit P extra N	1^{k} 000	1^{k} 000
Cadmium Red GG	1^{k} 800	1^{k} 800
Cadmium Red G	0^{k} 400	0^{k} 400
Kaolin	-	15^{k} 000
Vultamol-Solution	10^{k} 000	10^{k} 000

Cure in hot water: 20 minutes at 110° C.

The following is another latex Mix for the above:

Latex Dry Rubber Substance	100^{k} 000
Colloid Sulphur	1^{k} 500
Vulkazit P	0^{k} 600
Vulkazit 774	0^{k} 600

Colloid Zinc Oxide	....	1k 000
Sulphate of Barytes	....	45k 000
Red Iron Oxide 720	....	5k 000
Vultamol-Solution	....	10k 000
Latekoll	....	as required

Cure in hot air: 60 to 70 minutes at 70° C.

Rubberising of cotton bags with latex can be carried out on a large scale. For this purpose, the cotton fabric must be coated on either side first with a thin layer of rubber dissolved in a solvent and then with a self-vulcanising latex compound. The advantages of using rubberised fabric in the manufacture of bags are threefold:

1. The loss of any fine material through the interstices of the fabric is rendered quite impossible.

2. When suitably composed, the latex coating will protect the bag from any corrosive action which its contents may engender.

3. In the case of goods for despatch by sea, the latex coating will protect the contents of the bags against the destructive action of sea water.

Rubberised bags are made in just the same way as ordinary bags, except that they are made of cotton, but the stitchings are coated with a self-vulcanising latex compound. Bags rubberised in this way have proved to be more durable than ordinary cotton bags.

The following trials have established the indisputable superiority of the rubberised bags compared with the ordinary ones, both made of the same quality of cotton fabric.

An unrubberised cotton bag and a rubberised one were filled with 1 cwt. of Ilmenite and were thrown from a height of 20 ft. on to a cemented floor. After one fall, the unrubberised bag broke to pieces, whilst the rubberised one sustained the trial 16 times. Several bags were tried in this way, with always the same result. In some cases, it was the stitching of the rubberised bag which gave way.

Mattresses made from Latex combined with horse hair or fibre are most suitable for tropical climates and are re-commended for hospital use. For this purpose, the fibre or the hair, as the case may be, is mixed as loosely as possible with a suitable self-vulcanising latex compound, they are spread 2″ high in a frame of the exact shape of the mattress and allowed to dry, the vulcanisation being effected in a few days' time, after which the hairs or fibres stick together, forming a mass firmly adhering, the resilience of which, without doubt, is very satisfactory. After vulcanisation, the mattress can be covered with a cotton envelope and is ready for use. The life of these mattresses is far longer than that of ordinary mattresses and they are also more comfortable.

The following mix is suitable both for rubberising fabric for bags and as a latex compound for producing mattresses combined with fibres or horse hair.

Latex concentrate (60%)	100^{k} 000
Colloid Sulphur	6^{k} 000
Colloid Zinc Oxide	1^{k} 000
Aresklene	1^{k} 000
RN 2	1^{k} 500
Distilled Water	As required
Dyes	As required

Self-vulcanising in room temperature in 14 days or in hot air at 100° C. in 5 to 10 minutes.

Sponge Rubber made from Latex. In Part II we have seen how sponge can be manufactured from milled rubber. For that purpose the rubber is softened as much as possible by masticating it twice or thrice on heated rollers. No doubt such a treatment destroys the elasticity of the product, but on the other hand facilitates the blowing up of the compound during vulcanisation. Generally a blowing up agent is mixed with the compound beforehand.

The first attempts to produce sponge rubber from latex were carried out about thirty years ago. A porous coagulum was made by mixing gas-creating-ingredients with the latex compound during its coagulation. The product was then filled in moulds and cured either in the press or in the vulcanising pan.

From the various trials made it was found that the best method of obtaining the sponge paste was by whipping the latex compound with all the required fillers and vulcanising agents so as to produce a foam.

Foaming agents like soap in solution capable of exercising a retarding effect on the coagulation should be added to the compound, which is thoroughly whipped with a sort of egg-beater. The required coagulating agents should also be added to the foam so produced which is then immediately filled in moulds to prevent any settling of the product taking place.

The moulds must be tightly closed so that the water contained in the foam may not escape. The product is so vulcanised, after which the sponge rubber is removed from the mould and allowed to dry after having been thoroughly washed.

Mattresses and other *upholstery requisites* like *seat cushions* can also be made from sponge rubber, the thickness of which should not exceed one inch, as otherwise difficulties may arise in connection with the drying of the vulcanised product.

The following compound is recommended in *Latex in Industry* for the fabrication of sponge rubber by the above mentioned method.

Latex Rubber	100^{k} 000
Sulphur	3^{k} 000
Accelerator ZDC	0^{k} 700
Mineral Oil	5^{k} 000
Caustic Potash	0^{k} 400
Casein	0^{k} 100
Oleic Acid	0^{k} 500

This compound, says Royce J. Noble, is sufficiently viscous to prevent settling of any ingredients. It contains about 65% solids and has an ammonia content of 0.05 to 0.1%. The latex mix is whipped until the desired density of froth is obtained. Sodium Silicofluoride is added as a 50% dispersion of the foam, the amount used depending upon the ammonia content, but being, as just said, in the order of 0.5 to 1.0%. After adding the Sodium Silico fluoride, heating is continued for a few minutes and the foam is then poured into metal moulds. The moulds are closed and immersed in hot water to jell and cure the foam. If desired, the moulds may be equipped with internal heating elements. The time of cure, using the accelerator stated, will be about 30 minutes, at 100° C.

We have seen in all the formulas for latex compounds that distilled water is needed for preparing the mixes. The question has been raised whether water collected from latex after it has been concentrated could be used instead of distilled water. In our opinion there should be no snags in the use of the waste liquid for wetting the compounding ingredients, provided a small amount of synthetic type of wetting agent as well as stabilising agents are added to the compound. No doubt the creaming agent used will ultimately be present in the latex, which may result in making it rather soft and sticky, which qualities are required for obtaining a good coating compound. But by using the water coming from the creaming of the latex, all of its natural constitutents are re-incorporated in the mix, and thus such compounds, after the water has finally evaporated, will be constituted of what we know as a *whole latex rubber*, the drawback of which, due to the water-soluble materials and stabilisers used for the concentration process, is that the rubber film after the water has evaporated will be of poor resistance to water absorption. This is not, of course, of much consequence when the latex compound is to be used for coating purposes, but is a serious defect when it is used for insulating cables, for which a rubber compound with the least possible concentration of water soluble ingredients is required, so that the insulating resistance may be as high as possible.

So in conclusion, let us suggest that water coming from the concentration of latex can be advantageously used instead of distilled water for the preparation of various latex compounds with the exception of those compounds specially composed for insulating electrical cables and wires.

The End.