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MANUFACTURE OF RUBBER

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This invention concerns the manufacture of shaped articles of soft vulcanized rubber possessing a high and variable degree of flexibility and resilience and an improved resistance to oil absorption.

According to the invention, a shaped vulcanized soft rubber article is produced, which is characterized by the presence therein of a high proportion of an oleaginous softener, that is to say, an oily or fatty substance normally fluid or of low melting point.

The invention has particular reference to an improved manufacture of printers' rollers and like printers' devices.

The usual printers' rollers of gelatine composition have a number of disadvantages, notably uncertainty of life and sensitivity to changes in atmospheric humidity and temperature; and the proposal has been made to replace the gelatine by vulcanized rubber associated with rubber substitute (pre-vulcanized unsaturated fatty oil) and the usual compounding ingredients, this alternative aiming at providing a roller of greater permanence and of increased oil-resisting properties. In this alternative there is a limit set in practice to the proportion of rubber substitute and consequently to both the variability in the softness and the degree of oil-resistance of the product. The present invention provides a printers' roller of improved resistance to atmospheric changes, a wider variability in resilience and softness and increased resistance to oil-absorption. Such rollers and the like also do not need the constant cleaning which is necessary in the case of similar articles of gelatine.

A shaped article of soft rubber, for example, a printers' roller, according to this invention may comprise or consist of a vulcanized plastic provided by a vulcanized mixture of rubber and a high proportion of oil or derivatives thereof.

The softener may be a mineral oil or an appropriate low-melting derivative such as mineral jelly, or a mineral oil in association with said type of derivative; or may be an animal or vegetable oil, or a mixture of mineral and fatty bodies. Since permanency is a quality to be desired in the product, the softening agent should be one which is substantially non-volatile between reasonable temperature ranges. Substantially non-volatile hydrocarbon oils meet this condition, examples of suitable oils of this class being transformer oil and lubricating oils, especially spindle oil. It has been found that hydrocarbon oil fractions, such as kerosene, which contain components volatilisable on comparatively

moderate rise of temperature, while capable of giving primarily a rubber composition of the type characterising the present invention, possess the disadvantage just mentioned by reason of loss with time of at least a part of the oil component with a consequent shrinkage of the product.

Palm oil and olive oil are examples of suitable vegetable oils. Vegetable oils of solid character, such as palm oil, tend, if used alone in high proportion, to give rather hard final products, and in such cases there may be a practical limit set to the quantity of oil utilisable alone. For example, 100 per cent. (relatively to the rubber) of palm oil alone gives a rather hard moulded product when the mixing is vulcanized under the conditions usually employed to produce soft rubber. Hence such a softener is unsuitable when used by itself, and it may be necessary to use oils and other softeners of the character of palm oil in conjunction with other softeners of more fluid nature. The production of over-hard products tends also, but in a higher degree, to follow the use of high melting point waxes and solid fats and fatty acids.

The type of composition according to this invention may possess the property, derived from the presence of an adequately high proportion of oleaginous softener, that they can be cast at ordinary temperature or at a comparatively low raised temperature, that is one not much exceeding 100° C., in the form of a parent mixing compounded from solid rubber. It will be appreciated, however, that the ease of moulding the mother-composition may be influenced by the character and content of the other ingredients of the mixing.

One type of composition according to this invention consists of a vulcanized product characterised by great softness combined with a high degree of resilience, and such material is especially applicable to the manufacture of face-masks, surgical pads, children's toys, soft rubber linings, coatings and cushions, sound and shock absorbers, and other articles wherein a high measure of softness and resilience are desiderata. The flexibility of these products and the fact that they can be made of very varying degrees of softness render them especially suitable for different kinds of surgical pads and like uses. The harder bodies are suitable for inking rollers for printers, and other uses for which the softer known rubbers are employed. Both types of material are particularly applicable to cases wherein the rubber is liable to come into contact with oil.

The compositions according to this invention may comprise fillers, which may be mineral or organic, and also colouring matter and other components such as are known in the art; and the final composition may be porous or micro-porous, opaque or translucent.

The invention comprises a process of manufacture of shaped soft rubber articles which is characterised by directly compounding rubber with an oleaginous softener in high proportion and with vulcanizing agents, with or without other ingredients as aforesaid, shaping the mixing, under application of moderate heat as required, and vulcanizing the mixing.

Vulcanization may be effected in the open and, by aid of suitable accelerators, at comparatively low temperature, i. e. one not substantially exceeding 100° C. but may be also carried out under pressure and high temperature.

According to one embodiment of said process of manufacture, solid rubber is directly compounded to a homogeneous mass with an oleaginous softener in high proportion and with vulcanizing agents, together with such other components as are desired, and the mixing is shaped and vulcanized.

Alternatively, the rubber may be in the form of an aqueous rubber dispersion, such as rubber latex; and in this case an emulsifying agent may be employed for the better homogenisation of the aqueous material and the softener.

The use of an aqueous rubber dispersion has the advantage that all the constituents of the primary mixing can be free-flowing at room temperature. The mixing can therefore be very easily filled into a mould and air-pockets can be readily eliminated. Care must, of course, be observed that the rubber dispersion does not coagulate appreciably before it is introduced into the mould. The use of ingredients in dispersed form, as, for instance, an emulsion of the softener in rubber latex, has several advantages over dry mixes in that, the dispersions being naturally free-flowing, ingredients, including softeners, solid at ordinary temperatures can be used without adversely affecting the fluidity of the mixing. Thus, for example, emulsions comprising waxes and bitumens may be used with due allowance, as explained above, for the necessity of a limited proportion.

When ordinary raw rubber is used, it may be milled in the customary manner and directly dispersed with the aid of heat in the softener, with or without the usual compounding ingredients as may be desired, but the addition of the accelerator is preferably reserved to a separate stage. Since it is difficult to attain homogeneous dispersion of the rubber in the cold within a practicable time, the admixture with the softener is preferably effected under application of heat. The accelerator, which may conveniently be previously admixed with some softener, e. g. the same softening agent as compounded with the rubber, is subsequently added. The accelerator may also be introduced otherwise than distributed in a part of the softener, provided that uniform admixture with the main body of the materials is attained and risk of "scorching" is avoided. Likewise the other compounding ingredients may be added at any convenient stage, and may be worked in with the rubber or the softener in the first place or partly in the one and partly in the other.

The use of certain softening agents in rubber for the purpose of obtaining soft rubber and also for facilitating mixing has been known for a long time. Thus for the said purpose and also for the

production of materials for other specific ends, the addition of wax, such as paraffin wax and montan wax, with or without oil, has been proposed. In the ordinary use of true softening agents as previously known the maximum proportion relatively to the rubber may be said to be about 25 per cent. for special types of mixings such as are employed for sponge rubber, the usual proportion being about 5 per cent. or less. These considerations apply to the compounding of ordinary raw rubber. In the case of aqueous rubber dispersions, such as latex, the addition of oils likewise usually in comparatively small proportion, has also been proposed. The percentages in such cases have amounted to but not exceeded 100% on the weight of the rubber, as heretofore practised.

According to the present invention a very much higher proportion of oleaginous softener is introduced into the rubber than has hitherto been conceived to be possible or practicable. Such proportion, like that of other components of the mixing, may be varied over a wide range and no absolute numerical rule can be laid down, but as a practical guide it may be said that the lowest proportion of oleaginous softener, expressed relatively to the rubber, is such that, in contradistinction to known practice with raw rubber, the final mixing is unsuitable for feasible working on the ordinary mixing rolls. Thus, it has been found that with spindle oil the maximum amount which could be incorporated—although with difficulty—with 100 parts of rubber on ordinary mixing rolls was about 70 parts, and a somewhat higher proportion in the presence of 100 parts of mineral filler (equal weights of clay and whiting). The products were soft, sticky masses which, although easily shapable, could barely be cast by pouring up to a temperature of 110° C. For a mobile oil, such as spindle oil, therefore, a high proportion is to be regarded as upwards of approximately 70 per cent. relatively to the rubber, and larger proportions of more viscous softeners must be used to obtain mixings of like viscosity.

The variation in the proportions of the mixing components is, of course, to be determined by the physical properties of the final compositions desired; and the degree of softness to be sought may vary from that of what is technically known as soft vulcanized rubber to softer products such as some of the gelatine compositions now in use.

I have found that the advantages in printers' rollers manufactured from rubber compounded with a high proportion as aforesaid of oleaginous softener are not confined to compositions comprising a mineral oil or other individual oil alone. Not only by varying the proportion of softener, but also by varying the composition thereof, it is easily possible to obtain bodies of the different degrees of resiliency and softness previously indicated and always of much improved resistance to oil-absorption. When, according to this invention, a vulcanizable vegetable oil is employed, the oleaginous softener in the finished composition may consist of or comprise vulcanized oil; but the product is distinguished from that obtained by the incorporation of rubber substitutes with rubber in that said product will always contain a much higher proportion of oleaginous softener or even of vulcanized oil alone, the direct incorporation of the softener with the rubber followed by vulcanization of the mixture permitting the introduction of a much higher proportion of oil, with a consequent increase of oil-resistant properties in the product, wider variation in the degrees of softness,

and, in addition, greater facility of manufacture, since the parent mixing can be prepared fluid and hence be readily manipulated. It will be appreciated that these advantages of improved oil-resistance, variability of softness and greater ease of manufacture also apply to articles according to the invention which do not contain vulcanized oil.

It is readily possible by preliminary trial so to adjust the relative quantities of the mixing components as to give a mixing which, by reason of an adequately high proportion of softener, can be cast at moderate temperature (that is to say, between normal temperature and one not substantially exceeding 100° C.) and provide a final composition of a softness between the limits previously indicated. It will be appreciated that the temperature at which the mixing may be conveniently cast is not solely dependent upon the proportion of softener present since the nature and amount of the other compounding ingredients in the mixing may alter its degree of mobility, and consequently a higher temperature may be necessary in order to make the mass sufficiently free-flowing to be moulded under practical conditions. The pasty-like mixings referred to above are adaptable to such shaping methods as extrusion; but for ordinary mould-shaping the proportion of softener must be such as to render the mixing sufficiently mobile to fill the interstices of the mould and to find its own level at or below the temperature at which setting or vulcanization takes place. In most cases it has been found possible to use a mobile softener, such as spindle oil, and in such proportion that the mixing can be described as being at normal temperature a fluid rather than a plastic solid or a paste; but in other cases where it may be desired to reduce the proportion of liquid softener or to use a more viscous material or a normally solid substance, such as petroleum jelly or palm oil, the mixing may not be mobile at room temperature but may be a solid, a viscous or a pasty mass which flows readily only at artificially raised temperature—which may, with convenience, be adjusted to be that at which setting or vulcanization takes place. It will be clear that there is no limit to the fluidity or solidity of the oleaginous softener used provided that the mixing melts and becomes fluid so that it may be cast before setting or vulcanization begins.

The lower limit of temperature is conditioned only by that requisite to shape the mixing, and, if desired, also to effect setting or vulcanization. If the mixing itself be a liquid which will find its own level at room temperature the temperature to which the mixing is subjected need be no higher than that required to effect setting or vulcanization within the desired period.

It will be apparent, therefore, that the minimum amount of softener in the mixing will depend on (1) the viscosity, fluidity or mobility of the softener employed; (2) the temperature to which it is possible to heat the mixing before setting begins; (3) the particular accelerators of vulcanization and other vulcanizing ingredients which control the temperature at which setting begins; and (4) a time factor which is also dependent upon the vulcanizing ingredients.

The higher limit of temperature is restricted by the tendency to decomposition of the rubber or other ingredients of the mix, and the tendency to form gas pores or bubbles, which result in a porous product, although in some cases it is desirable to employ a higher temperature than is otherwise necessary in order to produce intentionally a porous product. It will, however, be obvious to those

skilled in the art that in most cases it is desirable to work at relatively low temperatures and to use powerful accelerators or combinations of these, as at higher temperatures gas bubbles will form more readily than in the known processes of vulcanizing in which the material is enclosed and vulcanization takes place under excess pressure.

The vulcanization of the parent mixing may, as already stated, be effected at low temperature and in the open by the known procedure of including ultra-accelerators in the mixing; and vulcanization under these conditions may be regulated by the combined use of a mixture of accelerators, for example, a reagent of a "semi-ultraaccelerator" type, an instance of which is mercaptobenzothiazole, in conjunction with a lower powered accelerator, such as diphenylguanidine, the combined effect being that of an ultraaccelerator of regulated power.

The following are examples of ways in which the invention may be carried into effect, but it is to be understood that these examples are given for illustrative purposes only and that the invention is not limited thereby.

Example I

A mixing as follows:—

	Parts by weight
Rubber.....	100
Sulphur.....	5
Zinc oxide.....	10
Palm oil.....	10

was made on the mill, and was then dispersed in 300 parts by weight of spindle oil with the aid of gentle heat, and to the dispersion thus obtained there were added, with uniform mixing of the materials during the addition, two parts by weight of diphenylguanidine and one part of mercaptobenzothiazole distributed in a little high-boiling naphtha.

The mixture, which was of a viscosity to allow of slow flowing at ordinary temperature, was poured into a round-bottomed basin and was vulcanized by heating in the open for 2 hours on a water-bath. The product was a buff-coloured, lenticular-shaped object, which was very soft but firm and resilient, and suitable for a surgical pad.

Example II

A mixing as follows:—

	Parts by weight
Rubber.....	100
Sulphur.....	5
Zinc oxide.....	20
Lithopone.....	10
Red colouring matter.....	0.0375
Palm oil.....	20

was worked up on the mill, and then dispersed in 300 parts by weight of spindle oil. To the dispersion were added, with careful mixing as before, two parts by weight of diphenylguanidine and one part by weight of mercaptobenzothiazole distributed in 10 parts by weight of spindle oil.

The product was a flesh-coloured viscous mass, very slow-flowing at the prevailing temperature but flowing readily on warming on the water-bath. The mixture was poured into an ordinary open cake-mould and was vulcanized on the waterbath at 100° C. as before. The product was flesh-coloured, soft—although somewhat firmer than the produce of Example I—and highly flexible.

Example III

A mixing as follows:—

	Parts by weight
Rubber-----	100
5 Zinc oxide-----	10
Palm oil-----	25

was worked on the mill and stirred into 5 parts by weight of sulphur distributed in 175 parts by weight of petroleum jelly over steam. One part by weight of diphenylguanidine and 0.5 part by weight of mercaptobenzothiazole were subsequently added. The mass, moulded to shape, was vulcanized by heating at 100° C. for 2 hours. The product was a soft, compact, firm and elastic vulcanized rubber of a brown colour, suitable for printers' rollers and like uses.

Example IV

20 A mixing as follows:—

	Parts by weight
Rubber-----	100
Sulphur-----	4
Zinc oxide-----	10
25 Palm oil-----	100

was worked up in an internal mixer, 2 parts of diphenylguanidine and 1 part of mercaptobenzothiazole being subsequently added. As already explained, this mixing was over-viscous by reason of the sole presence in high proportion of palm oil. A part of the mixing was put into a mould and allowed to spread into position while vulcanizing at 100° C. the total period of vulcanization being 1½ hours. The product was dull-brown in colour, and relatively hard and stiff, being nearly as hard as what is technically known as a soft vulcanized rubber. It was of a nature suitable for making solid rubber balls, printers' rollers, door-stops and like uses.

Example V

A mixing as follows:—

	Parts by weight
Rubber-----	15
45 Sulphur-----	1.5
Zinc oxide-----	1.5
Petroleum jelly-----	100.0
Diphenylguanidine-----	0.3
50 Mercaptobenzothiazole-----	0.15

was prepared and treated as in Example III, except that the time of vulcanization was 1½ hours. The product was of a light yellow colour, very soft and flabby, with a surface tending to become slightly sticky.

Example VI

An ultimate mixing as follows:—

	Parts by weight
60 Rubber-----	100
Sulphur-----	75
Zinc oxide-----	20
Whiting-----	100
Palm oil-----	50
65 Spindle oil-----	400
Zinc diethyldithiocarbamate-----	4.0

was moulded to shape and vulcanized at 100° C. for 16 hours. The material obtained was dark reddish-brown, slightly porous, flexible and deformable, and harder than any of the foregoing products and, although containing, as shown, a high proportion of softeners, somewhat brittle. During vulcanization, some oil sweated to the surface. This product is also particularly suitable as material for printers' rollers.

Example VII

An ultimate mixing as follows:—

	Parts by weight
Rubber-----	100
Sulphur-----	5
Zinc oxide-----	20
Lithopone-----	10
Red dye-----	0.04
Palm oil-----	25
Olive oil-----	325
Diphenylguanidine-----	2
Mercaptobenzothiazole-----	1
Zinc isopropylxanthate-----	3.0

was made up. The dispersion of the rubber in the olive oil was much slower than when mineral oil was used. The mixing was vulcanized at 100° C. for 3 hours. The product was flesh-coloured, very soft and flexible and had a somewhat sticky surface.

Example VIII

To a mixing as follows:—

Rubber latex (about 40 per cent. dry rubber)-----	c. c. 250	25
Sulphur-----	grams--	3
Zinc oxide-----	do----	20
Piperidine pentamethylenedithiocarbamate-----	grams--	0.5

there were added 150 c. c. of spindle oil and 10-20 c. c. of glycerine. An emulsion was formed on shaking. This was poured into an ornamental open mould, and was heated therein in a water-oven for 1 hour. The product was a pale yellow, solid, soft, elastic mass reproducing the shape of the mould. Some moisture was lost during the process.

Example IX

To 250 c. c. of rubber latex (about 40 per cent. dry rubber content) a few drops of concentrated ammonia solution (0.880) were added and then three parts of colloidal sulphur paste of 50 per cent. concentration, 5 parts zinc oxide and 0.5 part of piperidine pentamethylenedithiocarbamate. Into this mixture there were rapidly stirred 100 parts of cod-oil, and the mixture immediately cast in an open cake-mould, because it was found that coagulation set in rather rapidly. The mould was heated for 1½ hours at 90° C. There was obtained a product of biscuit colour which, although soft, was substantially firm and sharply moulded.

The products obtained according to both the immediately foregoing examples are suitable for printers' rollers and like devices.

If desired, instead of employing hot-vulcanization methods in the production of the rubber article, other known vulcanization processes may be used, for example, the cold cure process. Thus, a vulcanized product may be obtained by merely pouring a small quantity of undiluted sulphur chloride into the liquid oil-rubber mixture and stirring well. Upon casting the resulting mixture the latter sets in a short time to a vulcanized product closely resembling the products of the foregoing examples.

I claim:

1. A vulcanized compound composed of vulcanized rubber material compounded from raw rubber or rubber substitute, a non-volatile oleaginous softener, a reinforcing material such as zinc oxide, and hot-cure vulcanizing and accelerating ingredients sufficient to effect vulcanization of rubber, the combined proportions by

weight of said rubber and reinforcing material being less than the proportion of said softener and such that the mixture will flow under pressure, and the amount of softener not exceeding three times the weight of the rubber.

2. A vulcanized compound composed of vulcanized rubber material compounded from raw rubber or rubber substitute, a non-volatile non-drying oleaginous softener, a reinforcing material, and hot-cure vulcanizing and accelerating ingredients sufficient to effect vulcanization of rubber, the amount by weight of said rubber being substantially half the amount of the softener.

3. A vulcanized compound composed of vulcanized rubber material compounded from raw rubber or rubber substitute, a non-volatile oleaginous softener, a reinforcing material, and vulcanizing and accelerating ingredients sufficient to effect vulcanization of rubber, the combined amounts by weight of said rubber and reinforcing material being approximately half the amount of the softener.

4. A vulcanized compound composed of vulcanizable rubber-like material, a non-volatile oleaginous softener, a filling material, and hot-cure vulcanizing and accelerating ingredients sufficient to effect vulcanization of the rubber

material, the amount of said softener being sufficiently greater than the combined amounts of rubber material and filler to produce a mixture, before vulcanization, capable of being flowed into a mold.

5. A vulcanized compound composed of vulcanizable rubber-like material, a non-volatile oleaginous softener, a filling material, and hot-cure vulcanizing and accelerating ingredients sufficient to effect vulcanization of the rubber material, the amount of said softener being sufficiently greater than the combined amounts of rubber material and filler to produce a mixture, before vulcanization, capable of being flowed into a mold, and the amount of said filling material being less than the amount of rubber material.

6. A vulcanized compound composed of vulcanizable rubber-like material, a non-volatile oleaginous softener, a filling material, and hot-cure vulcanizing and accelerating ingredients sufficient to effect vulcanization of the rubber material, said rubber material being equal at least to one-third but not exceeding the amount of said softener whereby to produce a mixture before vulcanization which is sufficiently fluid to flow into the cavities of a mold.

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