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SOLVENT-BASED GASKETING COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Gasket-forming compositions for container closure elements comprised of a peptized curable polymer of 2-chloro-1,3-butadiene dissolved in a solvent having a minimum boiling point of 230° F., such as xylene and toluene. The compositions may be modified by the inclusion of additives, e.g., fillers, such as clay and plasticizers for the polymer, such as dioctyl phthalate. Illustrative curing agents include magnesium oxide, zinc oxide and mixtures thereof.

This invention pertains to elastomeric gaskets for closure elements. In particular, this invention relates to solvent-based elastomeric compositions useful in preparing sealing gaskets for aerosol mounting cups.

The use of pressurized aerosol containers in the packaging and dispensing of both fluid and powdered particulate material has grown considerably in recent years. Currently, a wide variety of products such as insecticides, paints, cosmetics, food products and pharmaceuticals are being marketed in aerosol-type packages. A typical aerosol unit comprises a hollow cylindrical container tightly closed at one end and is provided with an opening at its opposite end for receiving a dispenasing valve assembly. A metal mounting cup serves as a closure for the container and also as a support for the valve assembly which is tightly fitted within an aperture centrally located in the cup. At its outer edge, the mounting cup is adapted to be rolled and crimped to the walls forming the opening in the container and carries an annular gasket which forms a seal in the seam produced upon crimping.

The gasketing material used in aerosol mounting cups, as in other closure elements, should be elastic and resilient to the extent that it yields under deforming forces to establish a satisfactory seal when the cup is crimped to the container and to maintain an established seal over normal storage times. Also, the gasket should be resistant to the deteriorating effect of oils, solvents, acids, alkalis and other materials which may be present in the container contents. The resistance to deterioration is especially important in gaskets used in aerosol mounting cups because of the chlorinated and fluorinated compounds used as propellants for dispensing the container ingredients. In addition, the gaskets should be relatively thick, e.g., in the order of 30 mils, to provide tight seals on irregular finishes as frequently encountered in aluminum aerosol cans which are subject to deformation during handling.

Among the gaskets employed in aerosol mounting cups are those of the "flowed-in" type prepared from solvent-based rubber compositions comprising an elastomer dispersed or dissolved in a volatile organic solvent and may also contain pigments, fillers, curing agents and other compounding ingredients. Because of the superior resistance of neoprene to oxidation, oils and many chemicals, the compositions most widely used comprise neoprene, i.e., a chlorobutadiene polymer dissolved in a suitable solvent, such as benzene or methyl ethyl ketone, though the solvent conventionally employed is a mixture of toluene and petroleum naphtha. In preparing gaskets from these compositions, a band of the fluid material is deposited in the

sealing area of the mounting cup while the cup is being rotated beneath a metering nozzle through which the composition flows. Thereafter, the deposit is converted into a dry solid sealing mass by expelling the solvent at elevated temperatures.

While neoprene gaskets derived from these compositions have performed admirably in aerosol sealing applications, the compositions themselves have suffered from certain drawbacks. Because of the relatively low boiling solvents used and because a typical aerosol gasket, as compared to other closure gaskets, has a small surface area in relation to its thickness, it has been necessary to provide a long, slow drying cycle to prevent the formation of film defects which make the gasket unsuitable for use. Initially, a substantial portion of the solvent is removed from the deposit by air drying at ambient temperatures and thereafter, the temperature is gradually increased to remove the remaining solvent and to cure the composition. With the standard solvent mixture consisting of toluene and naphtha, six to seven hours has been required to remove substantially all of the solvent and to cure gaskets having a dried thickness between about 25 and 30 mils. Since the extent of blistering depends primarily upon the rate at which the solvent is expelled, attempts to hasten the drying operation by raising the temperature above the ranges customarily employed have been unsuccessful. The extremely rapid volatilization of the solvent under these conditions invariably results in blistering, if not in actual disruption of the film.

Because of the frequent appearance of bubbles in the elastomeric solutions, it has been the general practice to vacuum stir the compositions prior to lining. Otherwise, the deposit will have a greater tendency to blister even under standard drying and curing conditions. Besides being time consuming, vacuum stirring involves expensive equipment and usually causes a change in the total solids concentration as some of the solvent is removed from the composition. The degree of change in total solids concentration depends in large measure upon the solvent employed. For example, solvents having a relatively low boiling point or "low boiling ends" are volatilized quite rapidly under vacuum. The change in total solids concentration also depends upon the vacuum applied and the stirring time both of which vary considerably in commercial operations according to the equipment employed, the working condition of the equipment and the rate at which a batch of composition is used.

While the total solids may be accurately readjusted to the desired value by sampling the composition and calculating the difference between wet and dry film weights, this usually requires interrupting the stirring and lining operation at frequent intervals. In order to avoid this inconvenience and delay, it has been customary to estimate the amount of solvent needed to restore the composition to a selected total solids level and to add this amount to the batch from time to time. As a result, gaskets having a dry film weight above or below specifications may be produced before the variation is noted in the film weight checks made at the end of the drying and curing cycle. When this occurs, the number of gaskets outside of specifications is usually quite large due to the high lining speeds coupled with the prolonged dry-cure times.

Besides the above disadvantages associated with prior compositions, in general, there are certain problems peculiar to the use of solvent mixtures, such as toluene and petroleum naphtha. The gasketing compositions are difficult to manufacture since identical procedures often produce compositions exhibiting widely different flow characteristics at the same total solids concentration. Such compositions are also subject to further changes in viscosity as a result of vacuum stirring. This difference in flow characteristics has been found to result from an in-

crease in the proportion of toluene in the solvent mixture which causes a corresponding increase in viscosity. Because of the wide boiling range of petroleum naphtha, some of the low boiling ends escape from the composition during manufacture which causes an increase in total solids and leaves the composition rich in toluene. Since it is impractical in commercial operations to analyze each batch of composition for the change in the ratio of components in the solvent mixture, the standard mixture of toluene and naphtha is added to the solution to restore the total solids to a given value. Thus, on dilution with the standard solvent mixture the composition remains rich in toluene. During vacuum stirring additional low boiling portions of the naphtha are removed so that upon readjusting the total solids with the standard solvent mixture, the composition contains an even greater proportion of toluene than was originally present.

It has now been found that the disadvantages associated with prior neoprene solutions and with the preparation of aerosol gaskets from these compositions can be overcome by substituting relatively high boiling solvents for the low boiling solvents customarily employed. More specifically, the present invention provides a gasket-forming composition comprising a vulcanizable elastomeric polymer of 2-chloro-1,3-butadiene, a curing agent and a volatile organic solvent for the polymer, said solvent having a minimum boiling point of at least about 230° F.

By utilizing high boiling solvents, the compositions may be dried and cured in half the time previously required or less. For example, gaskets for aerosol mounting cups having a thickness (dry) up to about 35 mils may be dried and cured in four hours or less without the formation of blisters or other imperfections which impair the sealing efficiency of the gasket. The use of high boiling solvents also allows greater latitude during drying with respect to temperature control so that the compositions are able to withstand fluctations in temperature that would ordinarily result in unacceptable gaskets. In addition, the use of high boiling solvents eliminates the need for vacuum stirring and consequently, the equipment and time previously required for performing this operation. Also, the compositions are more uniform in flow characteristics upon manufacture and are less subject to changes in viscosity which greatly facilitates handling and allows greater ease in maintaining lining viscosities and total solids concentration within specifications.

The elastomeric polymers useful in preparing the compositions of the present invention include both homopolymers of 2-chloro-1,3-butadiene and copolymers of 2-chloro-1,3-butadiene with minor amounts of styrene, acrylonitrile, isoprene and other monomers copolymerizable therewith. As is well-known in the art, these chlorobutadiene polymers are commonly referred to as neoprenes and are commercially available as general-purpose types, such as GN, GNA, GRT, W, WRT and WHV. Any of the general purpose neoprenes may be used alone or in admixture. Also, special purpose type neoprenes, such as KNR, CG, and AC may be used in combination with the general purpose types.

Among the solvents suitable for use in the present invention are toluene, xylene and high boiling aromatic petroleum solvents, such as "Solvesso 100," with toluene being preferred because while it is high enough in boiling point to give the benefits of the invention, it is volatile enough to be completely removed in the drying operation, and because it yields compositions of usable viscosity at acceptable nonvolatile content. If desired, a mixture of volatile organic liquids which together form a solvent for the neoprene may be used. Also, a diluent may be used in conjunction with the solvent. It is essential, however, that each component used in the solvating medium have a boiling point of at least about 230° F. so that vacuum stirring may be eliminated and so that relatively thick, blister-free gaskets may be obtained at accelerated drying times.

The curing agent may be a metallic oxide, such as magnesium oxide, zinc oxide, lead oxides or mixtures of elemental sulfur with a metallic oxide. Preferably, the curing agent is a mixture of metallic oxides containing about four parts light or extra light calcined magnesia per five parts by weight of zinc oxide because such a mixture provides relatively rapid and complete cure with a minimum of scorching. If desired, a curing accelerator, e.g., 2-mercapto-2-imidazoline or p,p'-diaminodiphenyl-methane may be used in conjunction with the curing agent.

When a plasticizer is employed it may be dioctyl sebacate, dioctyl adipate, didecyl phthalate, dioctyl phthalate, naphthenic oils or any of the other relatively nonvolatile plasticizing materials used as processing aids for neoprene rubber. Though their use is not essential, plasticizers facilitate milling of the polymer with other ingredients, such as fillers, and also enhance the sealing characteristics of the resulting gasket.

While inorganic fillers are not essential in the present compositions, their use is preferred for aerosol purposes since they tend to reduce the permeability of the gasket to propellants. Also, fillers are helpful in modifying the specific gravity and flow characteristics of the fluid composition. Among suitable fillers which may be mentioned are hydrated calcium silicate, fine particle whitings, talc, precipitated silicon dioxide and clays.

Also, it is preferred to use a peptizer for the polymer particularly, where the total solids concentration is above about 50% by weight. Peptizers allow greater ease in adjusting the viscosity of the composition to a value within the range required for standard lining machinery. Typical peptizers include alkyl thiuram disulphides, e.g., tetramethyl and tetraethyl thiuram disulphides; piperidinium alkyl dithiocarbamates, e.g., piperidinum pentamethylene dithiocarbamate; and guanidines, e.g., di-o-tilylguanidine.

Other ingredients which may be incorporated into the composition are lubricants, e.g., stearic acid and petroleum waxes; antioxidants, e.g., diphenyl-p-phenylenediamine and p(p'-tolylsufonylamido)diphenylamines; and pigments, e.g., carbon blacks, iron oxides and titanium dioxide.

The amount of plasticizer used may range between about 0 to 200 parts by weight per 100 parts by weight of polymer. When added in amounts above about 200 parts, the plasticizer has a tendency to exude from the cured composition. Preferably, the plasticizer is used in amounts between about 40 and 60 parts by weight to give gaskets having the requisite degree of hardness to insure satisfactory sealing.

When fillers are employed, the quantity may range between about 0 and 300 parts by weight based on 100 parts by weight polymer. Above about 300 parts, the gasket becomes too hard and lacks the resilience and elasticity desired for sealing purposes. Generally, amounts ranging between about 80 and 200 parts are preferred, though the exact quantity used will depend upon the selected filler or combination of fillers and the characteristics they impart to the fluid composition and also, the properties they impart to the cured gasket.

Peptizers and the curing agent are used in amounts between about 0.5 and 6 parts and 1 to 10 parts by weight, respectively, as based on 100 parts by weight of polymer. When antioxidants, lubricants and other ingredients are employed, they are used in conventional amounts to achieve the desired effect.

The liquid organic solvating medium is used in amounts that will give compositions having a total solids concentration between about 40 and 75 percent by weight and preferably, between about 50 and 65 percent by weight. The total solids portion of the composition includes the combined weight of polymer, fillers, curing mixture and the other substantially nonvolatile ingredients used. Below about 50 percent total solids, it is difficult to obtain the thick gaskets required for aerosol mounting cups at a

single pass through the lining machinery. Above about 65 percent, the composition becomes quite thick and it is difficult to maintain the viscosity in a range that can be lined on conventional automatic lining machinery.

The following examples are given to further illustrate the present invention. All quantities given are in parts by weight unless otherwise specified.

EXAMPLE 1.—MASTERBATCH

Ingredients:	Parts by weight
Poly-2-chloro-1,3-butadiene	100
Sodium acetate (processing aid)	1.5
Paraffin wax, melting point 117° F. (lubricant)	2.0
Buca Clay (filler)	99.8
Dioctyl phthalate (plasticizer)	48.7
Light calcined magnesium oxide (curing agent)	4.0
Zinc oxide (curing agent)	5.0
Tetraethyl thiuram disulfide (peptizer)	2.5
Piperidinium pentamethylene dithiocarbamate (peptizer)	2.0
Zinc resinate, 1.6% by weight in dioctyl phthalate (wetting agent)	2.0
Precipiated silicon dioxide (filler)	0.1

The polymer, paraffin wax, sodium acetate and about 80 parts of the clay were milled together on a two-roll rubber mill. A blend containing the magnesium oxide and small portions of dioctyl phthalate and zinc resinate solution were then added to the rubber mix. After a smooth working sheet was obtained, the batch was transferred to an internal type of mixer. Another blend containing the silicon dioxide, zinc oxide, a small portion of plasticizer and the remaining zinc resinate solution was then added along with the peptizers and the remaining clay and plasticizer. After mixing of the batch was complete, the batch was divided into two portions.

(A) One portion was solvated in a mixture of toluene, which has a boiling point of about 232° F., and petroleum naphtha, which has a boiling range of between about 115° F. to 238° F. The toluene was used as a solvent for the polymer and the naphtha was used as a diluent. The ratio of toluene to petroleum naphtha was 3 to 1 parts by weight, respectively.

(B) The other portion was solvated in toluene alone. The total solids concentration of the compositions prepared in (A) and (B) was approximately 57% by weight.

Both of the compositions, (A) and (B), were lined in the laboratory in standard aerosol mounting cups using conventional automatic lining machinery. The quantity of composition used in each cup was about 525 mgs. wet film weight, and the cups were lined at conventional rates of about 150 per minute. Neither composition was vacuum stirred before lining.

The lined cups were then dried and cured according to the following standard laboratory schedule.

1 hour—Air dry (approx. 70° F.)
1 hour—155° F.
1 hour—200° F.
1 hour—325° F.

The gaskets prepared from composition (A) had a thickness of between about 25 and 30 mils. From an examination of the lined cups it was found that 75% of the gaskets prepared from (A) were blistered and unsuitable for use.

In comparison, it was found that all of the gaskets prepared from composition (B) were suitable for use and like the gaskets prepared from composition (A) had a thickness between about 25 and 30 mils.

The performance of compositions (A) and (B) were further compared by drying and curing lined cups in commercial runs using a typical seven-hour drying cycle consisting of two hours air dry at room temperature and one hour each at 150° F., 200° F., 250° F., and 350° F. It was found that composition (A) showed sporadic blistering during the long dry-cure cycle even when vacuum stirred prior to lining while composition (B) gave 100% acceptable gaskets in the absence of vacuum stirring.

EXAMPLE 2

Another batch of composition identical to composition (B) of Example 1 was prepared as described above and used to line standard mounting cups in commercial, full-scale production runs. The quantity of composition deposited in each cup ranged between about 400 and 500 mgs. wet film weight, and the composition was lined without prior vacuum stirring.

The lined cups were divided into two groups. One group was dried and cured according to four-hour schedule (1) below. The other group was dried and cured according to the two hour and fifty minute schedule (2) wherein the air dry step was reduced to 30 minutes.

(1)	(2)
1 hour—Air dry (approx. 70° F.)	30 min.—Air dry
1 hour—150° F.	35 min.—120° F.
1 hour—250° F.	35 min.—160° F.
1 hour—325° F.	35 min.—225° F.
	35 min.—290° F.

Upon inspecting the resulting cups, it was found that all of the gaskets prepared according to schedules (1) and (2) were free from blisters and other imperfections and that curing in all cases was complete including the gaskets obtained from the 500 mg. deposits.

EXAMPLE 3

A masterbatch identical to that of Example 1 was prepared in the same manner described above.

The batch was solvated in xylene (boiling range approximately 275° to 295° F.) with simple stirring, and the total solids concentration of the resulting solution was adjusted to 57% by weight.

The resulting composition was lined without prior vacuum stirring in standard aerosol mounting cups using conventional nozzle-lining machinery. The quantity of composition deposited in each cup was about 525 mgs. (wet weight).

The lined cups were then dried and cured according to the following schedule.

1 hr.—Air dry
1 hr.—155° F.
1 hr.—200° F.
1 hr.—325° F.

Upon inspecting the cured linings, it was found that all of the gaskets obtained were blister-free and completely cured.

EXAMPLE 4

A masterbatch identical to that of Example 1 was prepared according to the method described above.

The batch was solvated in a mixture of an aromatic petroleum solvent, "Solvesso 100" having a boiling range between about 320° and 345° F., and an aliphatic petroleum solvent, "Varsol #1" having a boiling range of between about 321° and 388° F. The ratio of aromatic to aliphatic solvent in the mixture was 3 to 1 parts by weight, and the total solids concentration of the resulting solution was approximately 57% by weight. The aliphatic solvent was employed as a diluent in this composition.

The solution was deposited without prior vacuum stirring in standard aerosol mounting cups using automatic nozzle-lining machinery. The wet film weight deposited in each cup was about 575 mgs.

The lined cups were dried and cured using a two-hour schedule consisting of one hour at 240° F. and one hour at 325° F. without air drying at room temperature.

All of the gaskets obtained were free from blisters and other defects and were completely cured.

From the foregoing examples and from the results obtained, it is apparent that it is difficult to obtain blister-free gaskets for aerosol mounting cups using elastomeric solutions containing low boiling solvents even when the composition is vacuum stirred prior to lining and dried and cured over prolonged periods at gradually increasing temperatures. In contrast, when relatively high boiling solvents are employed, the drying and curing cycle may be drastically reduced without the formation of blisters or other film defects. Also, with high boiling solvents the initial air dry step at room temperature may be reduced substantially or eliminated altogether and vacuum stirring, as previously required, may be eliminated without adversely affecting the film continuity of the resulting gaskets.

We claim:

1. A gasket-forming composition consisting essentially of 100 parts by weight of an elastomeric polymer of 2-chloro-1,3-butadiene, between 0.5 to 6 parts by weight of a peptizer, between 1–10 parts by weight of a curing agent, between 0 to 200 parts by weight of a non-volatile plasticizer for the polymer, between 0 to 300 parts by weight of a filler, and a volatile organic solvent having a minimum boiling point of at least 230° F., said solvent being present in an amount sufficient to provide the composition with a total solids concentration ranging between 40 and 75% by weight.

2. A composition according to claim **1** wherein the solvent is selected from the group consisting of toluene, xylene, and a mixture of an aromatic petroleum solvent having a boiling range between about 320° and 345° F. and an aliphatic petroleum solvent having a boiling range between about 321° and 388° F.

3. A composition according to claim **1** wherein the peptizer is selected from the group consisting of an alkyl thiuram disulfide and a piperidinium pentamethylene dithiocarbamate.

4. A composition according to claim **1** wherein toluene is used as a sole solvent.

5. A composition according to claim **1** wherein xylene is used as a sole solvent.

6. A composition according to claim **1** wherein the solvent is composed solely of a mixture of an aromatic petroleum solvent having a boiling range between about 320° and 345° F. and an aliphatic petroleum solvent having a boiling range between about 321° and 388° F.

7. A composition according to claim **1** wherein the total solids concentration is between about 50 and 65 percent by weight.

8. A gasket-forming composition consisting essentially of 100 parts by weight of a vulcanizable elastomeric polymer of 2-chloro-1,3-butadiene, about 100 parts by weight of an inorganic filler, about 50 parts by weight of a plasticizer for the polymer, about 5 parts by weight of a peptizer for the polymer, about 10 parts by weight of a metallic oxide curing agent and toluene is used as the sole solvent for the polymer, said composition having a total solids concentration between about 50 and 65 percent by weight.

9. A composition according to claim **8** wherein the plasticizer is dioctyl phthalate and the curing agent is a mixture of zinc oxide and magnesium oxide.

10. A composition according to claim **9** wherein the filler is clay and the peptizer is a mixture of tetraethyl thiuram disulfide and piperidinium pentamethylene dithiocarbamate.

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