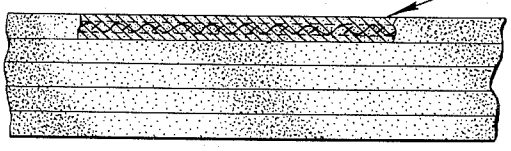
Jan. 29, 1957 R. W. BUCHANAN ET AL 2,779,687

FUEL PUMP DIAPHRAGM AND PROCESS FOR MAKING SAME

Filed Aug. 20, 1951



INVENTORS
Ross W. Buchanan &
BY John Gold
Willis, Helwig & Baillio
ATTORNEY

United States Patent Office 2,779,687 Patented Jan. 29, 1957

2,779,687

FUEL PUMP DIAPHRAGM AND PROCESS FOR MAKING SAME

Ross W. Buchanan and John Gold, Flint, Mich., assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware

Application August 20, 1951, Serial No. 242,784

10 Claims. (Cl. 117—47)

This invention relates to diaphragms such as are used in pumps for feeding gasoline and other liquid fuels to automobile engines and the like. More particularly, this invention relates to improved fuel pump diaphragms of the coated cloth type and to a process for manufacturing such diaphragms.

The conventional types of fuel pump diaphragms in use today consist generally of a cloth coated with some flexible and impervious material. These diaphragms must be strong enough to withstand repeated flexings and must be coated in such a manner as to be impervious to air as well as gasoline or other liquid fuels. It is also necessary that such diaphragms retain their flexible properties under a wide variety of operating conditions as, for example, high and low temperatures and high and low humidity.

Because of the variety of the fuels used in the various aircraft and automobile engines, each of these fuels having its own solvent properties, and because of the great variety of temperature and humidity conditions encountered in the operation of the various types of engines in various climates, it has been a general practice to choose the cloth coating material for the diaphragm according to the specific use to which the diaphragm is to be put. Thus, while one particular coating material may be quite insoluble in and therefore suitable for use with the aromatic hydrocarbon type fuels, it may on the other hand be too soluble in those fuels which contain aliphatic hydrocarbons or alcohols. Again, while one type of coating material may be quite flexible at ordinary temperatures, it may be quite inflexible at the very low temperatures, i. e. —70° F., which are encountered under some operating conditions. Then, too, while a particular diaphragm coating material may be quite resistant to deterioration during storage or operation at low humidity, it may be quite susceptible to deterioration at high humidity.

This invention has as an object the provision of a fuel pump diaphragm which is insoluble in and therefore suitable for use with any of the ordinarily used automotive fuels, i. e. aromatic hydrocarbons, aliphatic hydrocarbons, alcohols, esters, etc.

Another object of this invention is the provision of a fuel pump diaphragm having great flexibility and a long flex life under both high and low temperature operating conditions.

Another object of this invention is the provision of a fuel pump diaphragm which is highly resistant to deterioration during storage under adverse conditions with respect to humidity and temperature.

Another object of this invention is to provide a process for manufacturing diaphragms having the above mentioned qualities.

Other objects and advantages of our invention will more fully appear from the following description of preferred embodiments of our invention and from the drawing which shows a side view in partial section of a portion of a diaphragm made in accordance with the invention.

Among the various types of coating materials which have been proposed for use on fuel pump diaphragms are

mixtures of various bodied drying oils such as linseed and tung oils, certain of the phenolic resins such as, for example, phenol formaldehyde, and elastomers such as butadieneacrylonitrile copolymer, 2-chloro-1, 3-butadiene polymer, etc. None of these, however, is suitable under all operating conditions and for use with all types of automotive and aviation fuels. The elastomer 2-chloro-1, 3-butadiene, commercially available under the trade name Neoprene, has very low solubility in all of the various types of fuels and also has a high degree of flexibility throughout a relatively wide temperature range. However, there are a number of properties of neoprene which make its use as a fuel pump diaphragm coating material disadvantageous. Upon standing, for example, neoprene liberates minute amounts of hydrochloric acid, this action causing tendering of the fabric and eventually resulting in failure of the diaphragm. Also, layers of neoprene-coated fabric tend to stick together in areas where they are pressed. As long as the diaphragm assembly, which generally utilizes multiple layers of coated fabric, is not disturbed, sticking in the pressed areas is not a factor in the pump operation. However, in the course of a fuel pump inspection the diaphragm assembly is of necessity disturbed, thus resulting in a pulling apart of the layers which are stuck together, and thereby causing layer tearing and diaphragm failure. Moreover, the layers of neoprene-coated fabric tend to stick to each other even in the working area of the diaphragm where they are not pressed together, and this adhesion in itself contributes to diaphragm failure.

Another disadvantage of neoprene is its relatively high freeze point of —40° F. which precludes its efficient use when subjected to extremely low temperatures.

Perhaps the greatest disadvantage of neoprene diaphragms, however, is the fact that it is readily susceptible to scuffing. This scuffing of one layer of the diaphragm on another when the diaphragm is in operation removes appreciable amounts of the neoprene from these diaphragm layers, thus resulting in diaphragm failure.

In accordance with our invention, neoprene is used for fuel pump diaphragms in such a way as to take advantage of its desirable characteristics and on the other hand correct for those characteristics which are undesirable. This is accomplished by modifying the neoprene by the addition of copolymers containing vinylidene chloride. While vinylidene chloride-vinyl chloride copolymer serves as a suitable addition agent to modify and enhance the properties of neoprene insofar as its use for fuel pump diaphragms is concerned, we have found that the most suitable modifying composition is the copolymer of vinylidene chloride and acrylonitrile either with or without a plasticizer. Both vinylidene chloride-acrylonitrile copolymer and vinylidene chloride-vinyl chloride copolymer are in themselves too stiff and unflexible to serve as suitable materials for fuel pump diaphragms. However, when the copolymers of vinylidene chloride such as those mentioned above are combined either separately or in combination in suitable proportions with 2-chloro-1, 3-butadiene polymer, we have found that the properties of each complement each other so as to yield fuel pump diaphragms which are not only resistant to the solvent action of all of the commonly used fuels, but which are also capable of retaining flexibility throughout a wide temperature range. Such diaphragms are highly resistant to deterioration from heat and humidity while in storage and the layers have no tendency to adhere to each other as is the case when neoprene is used alone. The material is highly resistant to scuffing from the sliding action of one layer of the diaphragm on another, thus overcoming what is perhaps the greatest disadvantage of diaphragms using neoprene alone. The freeze point and other prop-

erties of the modified neoprene are such as to allow its efficient operation at extremely low temperatures.

Even when using neoprene by itself for a fuel pump coating material, it has been found desirable to use the elastomer in a vulcanized rather than an unvulcanized state. This is also true as regards the neoprenes which are modified as by this invention. Vulcanization adds toughness, tensile strength and other valuable properties to the material. If zinc oxide is used as the vulcanizing agent for the mixture, it serves not only in the capacity of a vulcanizing agent, but also in the capacity of an acid neutralizer for the finished diaphragm. Thus, the zinc oxide in the mixture neutralizes the minute amounts of hydrochloric acid which are liberated by the neoprene upon standing. It is, in this regard, generally preferable to add to the mix a slight excess of zinc oxide over that which is required for vulcanization.

It will be seen, therefore, that by utilizing the neoprene which has been modified by the addition of a copolymer such as vinylidene chloride acrylonitrile and into which has been incorporated zinc oxide both as a vulcanizing agent and as an acid neutralizer, all of the inherent disadvantages of neoprene as a fuel pump diaphragm material are avoided.

It is often desirable to incorporate in the coating a portion of carbon black or other suitable filler in order to give the coating greater strength. When carbon black is used as a filler it of course also serves as a coloring agent for the coating mixture.

We have found that a most satisfactory diaphragm material consists of from about 60 to 85 parts by weight 2-chloro-1, 3-butadiene, from about 15 to 40 parts by weight vinylidene chloride copolymer, from about 5 to 15 parts by weight zinc oxide, and from about 1 to 30 parts by weight of carbon black.

In our preferred modification we use a mixture consisting of about 70 parts by weight 2-chloro-1, 3-butadiene, about 30 parts by weight of a composition containing approximately 80% vinylidene chloride-acrylonitrile copolymer, and about 20% dibutyl phthalate plasticizer (sold under the trade name Saran F122A20), about 10 parts by weight of zinc oxide, and about 2 parts by weight carbon black.

It is to be understood of course that our invention is not limited to the specific ratios as set forth above, these only serving to illustrate more specifically our invention and the preferred range. It is also to be understood that the diaphragm material will of course contain small amounts of other materials used in the process of manufacture as described below. Thus, the diaphragm having the preferred ratio of about 70 parts by weight neoprene, about 30 parts by weight of the composition containing approximately 80% vinylidene chloride-acrylonitrile copolymer and 20% plasticizer, about 10 parts by weight zinc oxide, and about 2 parts by weight carbon black will of course also contain small amounts of anti-oxidant, accelerator, etc.

The copolymer used to modify the neoprene can be used with or without a plasticizer incorporated therein. While excellent diaphragms were obtained using as the modifying composition, vinylidene chloride-acrylonitrile copolymer containing no plasticizer (sold under the trade name Saran F122), the best results were obtained when either Saran F122A15 (vinylidene chloride-acrylonitrile copolymer plus 15% dibutyl phthalate plasticizer) or Saran F122A20 (vinylidene chloride-acrylonitrile copolymer plus 20% dibutyl phthalate plasticizer) were used as the modifying compositions for the neoprene. Of the latter two, we prefer to use Saran F122A20.

The conventional method of applying an elastomer coating to fabric or cloth is by a calendering process whereby a thin sheet of the elastomer is pressed into the cloth. We have found, however, that far better cloth penetration and cloth to elastomer adhesion can be obtained with our improved cloth coating compositions when application is made from an aqueous dispersion of the 2-chloro-1, 3-butadiene and the vinylidene chloride copolymer composition. Such an aqueous dispersion, which is usually referred to as a latex, consists generally of a suspension of the polymeric and copolymeric material in an ammoniacal aqueous medium containing stabilizing agents. When the suspension is applied to cloth under the proper conditions, the suspended polymers and copolymers coagulate out of the aqueous medium and onto the surface of the cloth fibers. While the application of the latex to the cloth can be accomplished by any convenient method, i. e. immersing or spraying, the immersion process proves most satisfactory since such a process affords easy control for attaining a uniform coating.

In order to effect greater penetration and better coating material to cloth adhesion we have also found that a pretreatment of the cloth with an aqueous solution of a wetting agent is most beneficial. Any suitable wetting agent can be used for this cloth pretreatment. We have obtained satisfactory results, for example, using an aqueous solution of a wetting agent bought under the trade name of Tergitol #7, and consisting generally of sodium salt of a higher secondary alkyl sulphate. We have also found such wetting agents as the dioctyl ester of sodium sulfo succinic acid (sold under the trade name Aerosol OT) and the sodium sulfates of the higher fatty alcohols (sold under the trade name Aquarex D) to be very satisfactory for the cloth precoating treatment.

Our preferred process for manufacturing the diaphragms of this invention is as follows:

The cloth which is to serve as the diaphragm base is first immersed in an approximately 1% aqueous solution of Tergitol #7 for about five minutes, the solution being maintained at about 200° F. It is then withdrawn from the bath and allowed to dry. The cloth used can be of any of the well known natural or synthetic fibers such as cotton or Nylon. We have used long staple Egyptian cotton airplane cloth with much success. Prior to treatment with the wetting agent the cloth can be dyed, with or without a prior bleach treatment, for identification purposes.

After the cloth is dried it is then immersed in the latex bath for a sufficient time to receive the desired thickness of coating, withdrawn and dried for about 30 minutes at 160° F. This step is then repeated three times, thus giving four separately dried coatings of the polymer-copolymer mix. It is to be understood that our invention is not restricted, however, to any particular number of coatings since it is often desirable to provide more or less than the four coatings which we use in our preferred modification.

The immersion is most advantageously effected by running lengths of the cloth through the bath by means of a conveyor system. The composition of the latex bath to produce a diaphragm of our preferred composition is as follows:

	Wet Basis, Parts by Weight	Dry Basis, Parts by Weight
Neoprene 571 latex (50% solids)	140.0	70.00
Emulphor ON (40% solids)	5.0	2.00
Sodium Silicate (10% solids)	2.5	0.25
Aerosol OT (3.5% solids)	1.4	0.50
Masterbatch (50% solids)	32.2	16.10
Saran F122A20 latex (53% solids)	56.6	30.0
Versene (10% solids)	3.3	0.33

The composition of the masterbatch is as follows:

	Parts by weight
Zinc oxide	65.20
Gastex	13.05
Accelerator A–1 (thiocarbanilide)	4.36
Sulphur	4.36
Neozone D	13.05
10% ammoniacal casein sol	30.00
10% Darvan solution	30.00
Water (soft or distilled)	40.00

The actual mixing is accomplished by adding to the neoprene latex with stirring the solutions of Emulphor ON, sodium silicate and Aerosol OT. Then the masterbatch dispersion is added. After the pH of the Saran latex is adjusted to 8 with a 5% sodium hydroxide, the Versene solution is added to the Saran latex. After thorough mixing of the Versene and Saran latex, it is added to the neoprene latex.

Emulphor ON and sodium silicate are stabilizers and the Aerosol OT is a wetting agent. Zinc oxide, thiocarbanilide and sulphur are necessary for the vulcanization of the neoprene. As has been stated previously, in addition to its role as a vulcanizing agent, zinc oxide acts also as an acid acceptor and prevents tendering of the cotton fabric. Neozone D is an anti-oxidant and Gastex is a semi-reenforcing carbon black used as a filler and coloring agent. The ammoniacal casein solution and the Darvan solution serve as dispersing agents.

In making up the masterbatch, the water, Darvan and casein are mixed together and the zinc oxide, Gastex, Accelerator A–1, sulphur and Neozone D are mixed so as to disperse the solids in the water phase. To effect the dispersion the masterbatch is milled for a minimum of 18 and preferably 24 hours in a ball mill.

The 10% ammoniacal casein solution is made by heating 86.75 parts of water almost to boiling, adding 1.5 parts of aqua ammonia, 0.25 part of a preservative such as Collatone and about 10 parts of a casein of high pH, i. e. 4.7 to 4.8.

The names used to designate the various bath constituents are in most instances the commercial trade names commonly used for their sale on the market.

The above described latex bath yields a diaphragm having a coating which contains approximately 70 parts by weight neoprene and 30 parts by weight Saran F122A20. It is to be understood that by changing the proportion of the latex constituents in the immersion bath, diaphragms containing varying ratios of neoprene and Saran and the other constituents may of course be obtained.

The cloth is passed through the latex bath at a rate of about 80 to 90 feet per minute. When the 70 parts neoprene-30 parts Saran latex bath described above is used, the dry weights in grams per square yard of the cloth tafer the first, second, third and fourth coatings are approximately as follows:

After—			
1st Coat	2nd Coat	3rd Coat	4th Coat
From 180 to 190 grams.	From 220 to 230 grams.	From 240 to 250 grams.	From 260 to 270 grams.

After the four successive coatings and dryign steps have been completed, the coated cloth is vulcanized. A typical vulcanizing operation is to heat the coated cloth for about thirty minutes at 250° F. The individual fuel pump diaphragms or diaphragm layers are then cut from the coated cloth. In the accompanying drawing, the diaphragm shown consists of a pluarlity of separate layers of the coated cloth.

While vulcanization of the coated fabric is not essential in all cases, this final step greatly improves the properties of the diaphragms. As was stated previously, vulcanization improves toughness and tensile strength. Vulcanized diaphragms also have better aging properties in that there is better retention of toughness and tensile strength.

The diaphragms resulting from our improved process and containing 2-chloro-1, 3-butadiene polymer modified by a copolymer containing vinylidene chloride, are greatly resistant to deterioration from high humidity and high temperatures. Because they are resistant to the solvent action of aromatic hydrocarbons, aliphatic hydrocarbons, alcohols, esters, etc., they can be used for pumping any of the conventionally used automotive and aircraft fuels. They retain their flexibility and are therefore useful at temperatures as low as —70° F. Because they are quite resistant to scuffing and peeling and because there is little tendency for the layers as shown in the accompanying drawing, to adhere to each other, these diaphragms are extremely durable even under adverse operating conditions.

While we have described our improved diaphragms in particular regard to their use in fuel pumps, we wish to point out that the diaphragms are also adapted to use in other types of pumps and in valves which operate on fluids or under conditions which make their use advantageous.

It is apparent that many widely different embodiments of our invention may be made without departing from the spirit and scope thereof and therefore it is not intended to be limited except as indicated in the appended claims.

We claim:

1. A diaphragm having high abrasion resistance, high and low temperature flexibility and resistance to the solvent action of hydrocarbon fuels and the like, said diaphragm comprising a cloth coated with a vulcanized mixture consisting essentially of from 60 to 85 parts by weight 2-chloro-1,3-butadiene polymer, from 15 to 40 parts by weight of a composition consisting of at least about 80% of a copolymer selected from the group consisting of polyvinylidene chloride-acrylonitrile and polyvinylidene chloride-vinyl chloride, and up to about 20% dibutyl phthalate plasticizer, plus carbon black as a coloring and reinforcing agent and zinc oxide in an amount sufficient to act as a vulcanizing agent and acid neutralizer.

2. A diaphragm having high abrasion resistance, high and low temperature flexibility and resistance to the solvent action of hydrocarbon fuels and the like, said diaphragm comprising a plurality of adjacent contacting layers of cloth, each of said layers of cloth being coated with a vulcanized mixture consisting essentially of from 60 to 85 parts by weight 2-chloro-1,3-butadiene polymer, from 15 to 40 parts by weight of a composition consisting of at least about 80% of a copolymer of polyvinylidene chloride and acrylonitrile and up to about 20% dibutyl phthalate plasticizer, plus carbon black as a coloring and reinforcing agent and zinc oxide in an amount sufficient to act as a vulcanizing agent and acid neutralizer.

3. A diaphragm having high abrasion resistance, high and low temperature flexibility and resistance to the solvent action of hydrocarbon fuels and the like, said diaphragm comprising a cloth coated with a mixture consisting essentially of from 60 to 85 parts by weight 2-chloro-1,3-butadiene polymer, from 15 to 40 parts by weight of a composition consisting of at least about 80% of a copolymer selected from the group consisting of polyvinylidene chloride-acrylonitrile and polyvinylidene chloride-vinyl chloride, and up to about 20% dibutyl phthalate plasticizer, from about 5 to 15 parts by weight zinc oxide and from about 1 to 30 parts by weight carbon black.

4. A diaphragm having high abrasion resistance, high and low temperature flexibility and resistance to the solvent action of hydrocarbon fuels and the like, said diaphragm comprising a cloth coated with a mixture consisting essentially of from about 60 to 85 parts by weight of vulcanized 2-chloro-1,3-butadiene polymer, from about 15 to 40 parts by weight of a composition consisting of about 80% vinylidene chloride-acrylonitrile copolymer and about 20% dibutyl phthalate plasticizer, from about 5 to 15 parts by weight zinc oxide, and from about 1 to 30 parts by weight carbon black.

5. A diaphragm having high abrasion resistance, high and low temperature flexibility and resistance to the solvent action of hydrocarbon fuels and the like, said dia-

phragm comprising a cloth coated with a mixture consisting essentially of from about 60 to 85 parts by weight of vulcanized 2-chloro-1,3-butadiene polymer, from about 15 to 40 parts by weight vinylidene chloride-acrylonitrile copolymer, from about 5 to 15 parts by weight zinc oxide, and from about 1 to 30 parts by weight carbon black.

6. A diaphragm having high abrasion resistance, high and low temperature flexibility and resistance to the solvent action of hydrocarbon fuels and the like, said diaphragm comprising a cloth coated with a mixture consisting essentially of approximately 70 parts by weight vulcanized 2-chloro-1,3-butadiene polymer, approximately 30 parts by weight of a composition containing about 80% vinylidene chloride-acrylonitrile copolymer and 20% dibutyl phthalate plasticizer, about 5 to 15 parts by weight zinc oxide, and about 1 to 30 parts by weight carbon black.

7. A process for manufacturing coated cloth diaphragms comprising the step of applying to the cloth an aqueous latex containing a mixture of polymeric material, zinc oxide and carbon black to thereby coat the cloth with said mixture, said mixture consisting essentially of (on a dry weight basis) about 60 to 85 parts 2-chloro-1,3-butadiene polymer, 15 to 40 parts of a composition consisting of at least about 80% of a copolymer selected from the group consisting of polyvinylidene chloride-acrylonitrile and polyvinylidene chloride-vinyl chloride and up to about 20% dibutyl phthalate plasticizer, about 5 to 15 parts zinc oxide and about 1 to 30 parts carbon black.

8. A process for manufacturing coated cloth diaphragms comprising the steps of applying to the cloth an aqueous latex containing a mixture of polymeric material, zinc oxide and carbon black to thereby coat the cloth with said mixture, said mixture consisting essentially of (on a dry weight basis) about 60 to 85 parts 2-chloro-1,3-butadiene polymer, about 15 to 40 parts of a composition consisting of at least about 80% of a copolymer selected from the group consisting of polyvinylidene chloride-acrylonitrile and polyvinylidene chloride-vinyl chloride and up to about 20% dibutyl phthalate plasticizer, zinc oxide in an amount sufficient to act as a vulcanizing agent and acid neutralizer and carbon black as a coloring and reinforcing agent, and thereafter vulcanizing said mixture.

9. A process for manufacturing coated cloth diaphragms comprising steps of treating said cloth with an aqueous solution of a wetting agent, applying to the cloth an aqueous latex containing a mixture of polymeric material, zinc oxide and carbon black to thereby coat the cloth with said mixture, said mixture consisting essentially of (on a dry weight basis) about 60 to 85 parts 2-chloro-1,3-butadiene polymer, and about 15 to 40 parts of a composition consisting of at least about 80% of a copolymer of vinylidene chloride and acrylonitrile and up to about 20% dibutyl phthalate plasticizer, zinc oxide in an amount sufficient to act as a vulcanizing agent and acid neutralizer and carbon black as a coloring and reinforcing agent, and thereafter vulcanizing said mixture.

10. A process for manufacturing coated cloth diaphragms comprising the steps of treating said cloth with an aqueous solution of a wetting agent, drying said cloth, immersing said cloth in an aqueous latex containing a mixture of polymeric material, zinc oxide and carbon black to coat the cloth with said mixture, said mixture consisting essentially of (on a dry weight basis) about 70 parts 2-chloro-1,3-butadiene polymer, about 30 parts of a composition consisting of about 80% of a copolymer of polyvinylidene chloride-acrylonitrile and about 20% dibutyl phthalate plasticizer, about 5 to 15 parts zinc oxide and about 1 to 30 parts carbon black, drying said cloth and thereafter vulcanizing said mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,005,637	Schidrowitz	June 18, 1935
2,019,420	Lejeune	Oct. 29, 1935
2,250,674	McBurney	July 29, 1941
2,255,834	Taylor	Sept. 16, 1941
2,405,038	Jennings	July 30, 1946
2,465,336	MacDonald et al.	Mar. 29, 1949
2,547,605	Signer et al.	Apr. 3, 1951