Jan. 4, 1955 N. L. GREENMAN ET AL 2,698,788

RUBBERIZED FIBROUS SHEET AND METHOD OF MAKING THE SAME

Filed Feb. 27, 1952

3 Sheets-Sheet 1

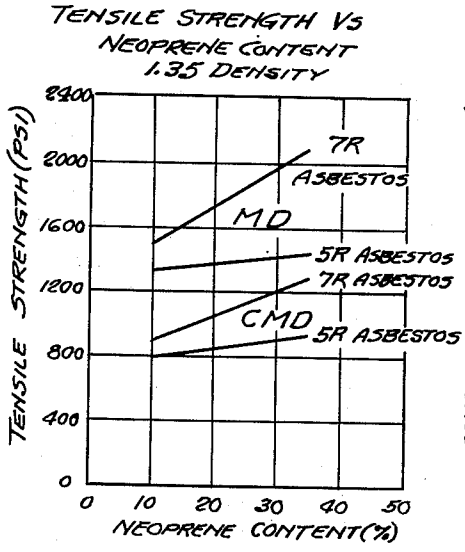


Fig. 1

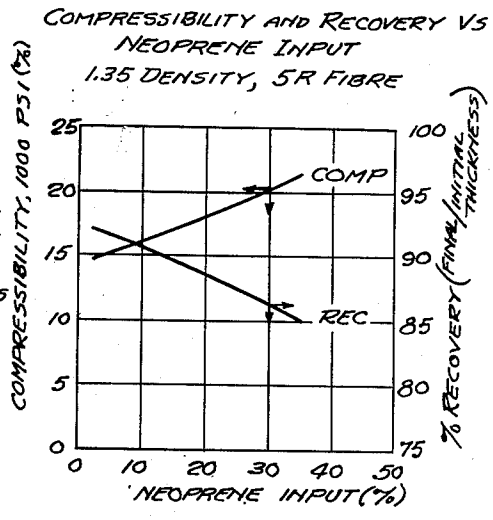


Fig. 2

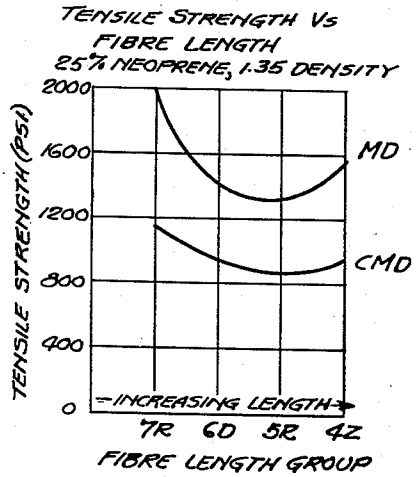


Fig. 3

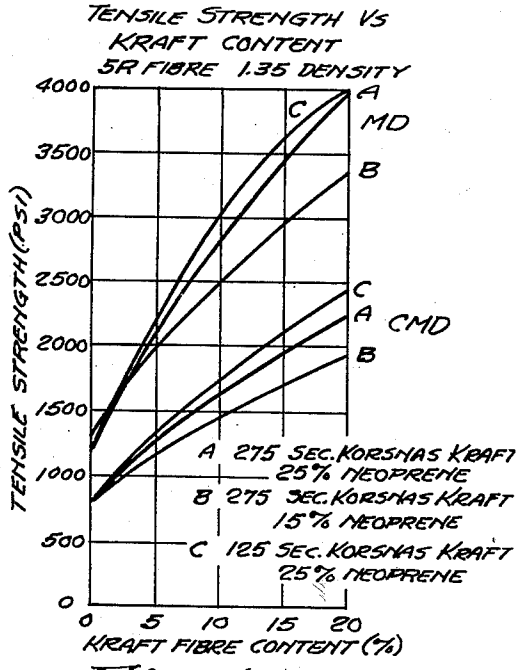


Fig. 4

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Jan. 4, 1955 N. L. GREENMAN ET AL 2,698,788

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Filed Feb. 27, 1952 3 Sheets-Sheet 2

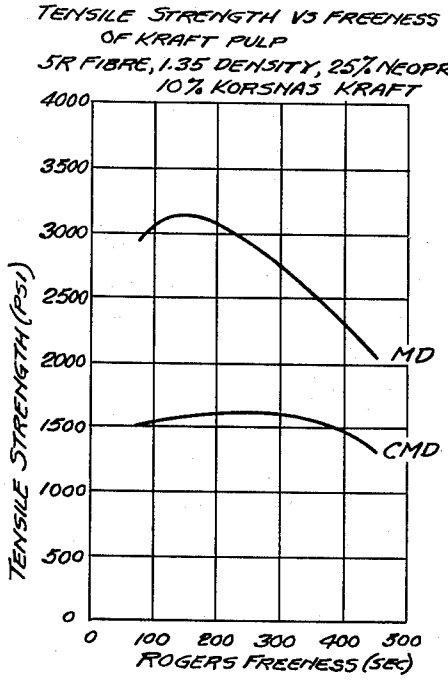


Fig. 5

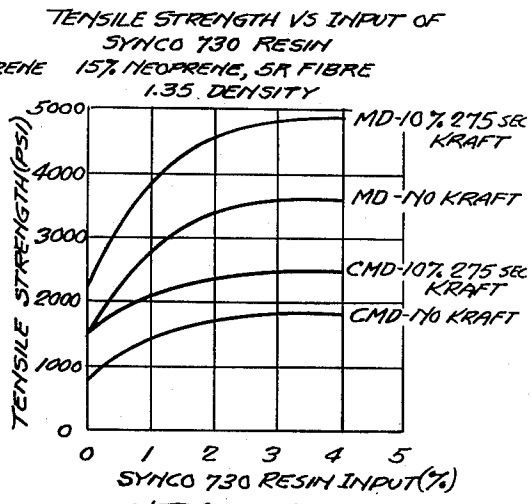


Fig. 6

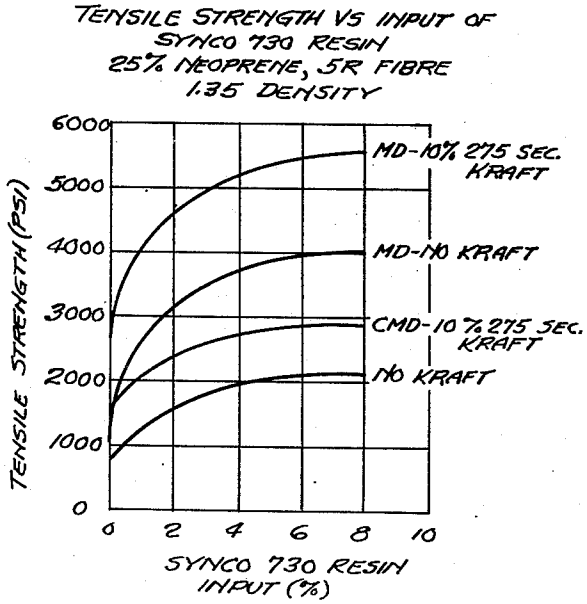


Fig. 7

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Jan. 4, 1955 N. L. GREENMAN ET AL 2,698,788

RUBBERIZED FIBROUS SHEET AND METHOD OF MAKING THE SAME

Filed Feb. 27, 1952 3 Sheets-Sheet 3

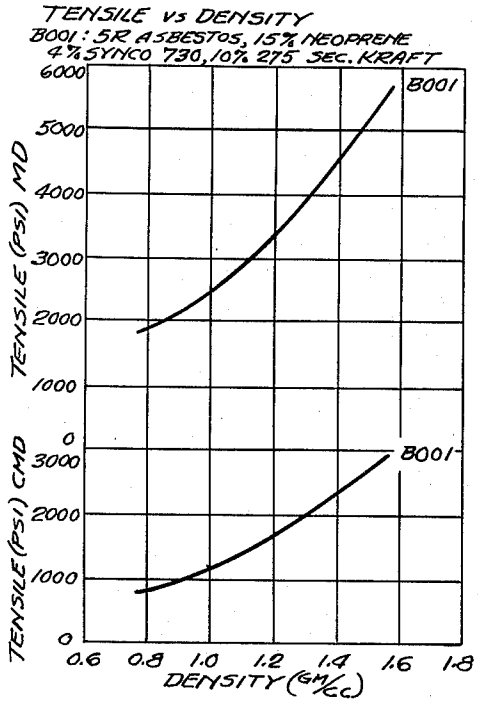


Fig. 8

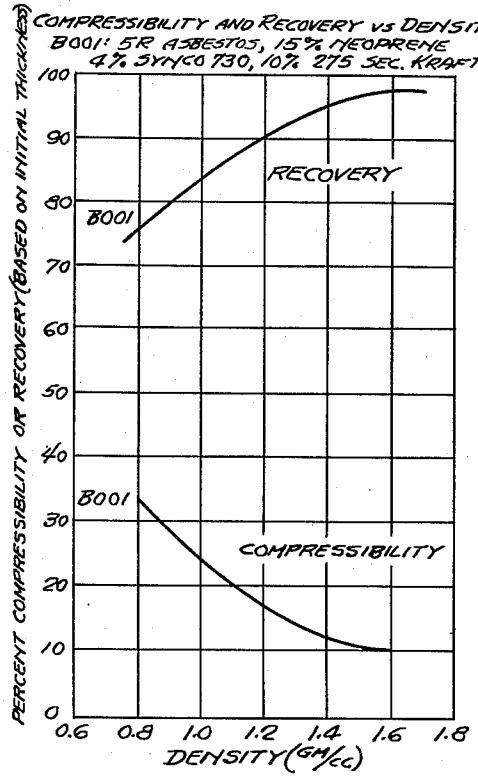


Fig. 10

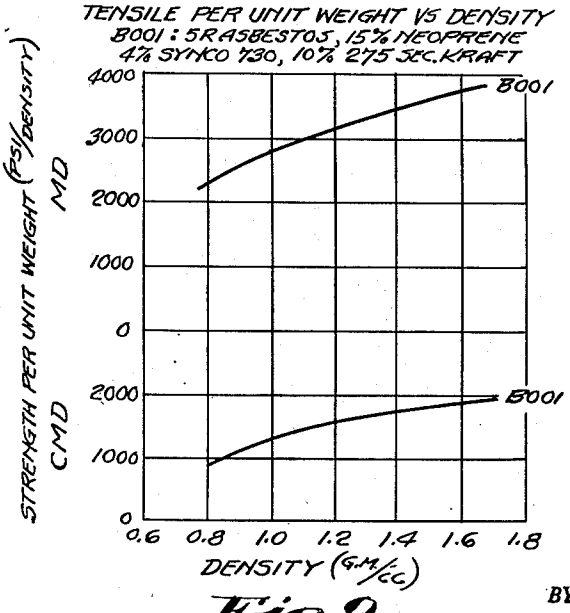


Fig. 9

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2,698,788

RUBBERIZED FIBROUS SHEET AND METHOD OF MAKING THE SAME

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Application February 27, 1952, Serial No. 273,747

11 Claims. (Cl. 92—3)

This invention relates to a process of making a rubberized felted fibrous sheet particularly useful for the production of gaskets and other uses and to the rubberized felted fibrous sheet produced by such process.

One object of the invention is to produce a rubberized felted sheet having unusual tensile strength and characterized by its compressibility under load and a substantial recovery upon removal of the load and by its resistance to such fluids as alcohol, water, gasoline, oils and the like.

A further object of the invention is to produce a fibrous gasket material in which the physical properties of the material as to tensile strength, compressibility, resistance to solvents and minimum swell when exposed to water enable the material to be used with advantage as an improved gasket material meeting the requirements and specifications of the automotive, aircraft and other industries.

A still further object of the invention is to provide a novel and highly efficient method for the production of the present novel rubberized felted fibrous sheet.

With these general objects in view and such others as may hereinafter appear, the invention consists in the novel process of producing a rubberized felted fibrous sheet having the physical and chemical characteristics above referred to and by which the material is rendered suitable for the production of gaskets and for various other industrial purposes, and in the product produced by such process, as hereinafter described and particularly defined in the claims at the end of this specification.

In the drawings, Figs. 1 through 10 are graphs illustrating the advantageous effects produced by the incorporation in the rubberized felted fibrous sheet produced in accordance with the invention of cellulosic fiber and beater addition phenol-formaldehyde resin, and also of the effects of variation in the character of mineral fiber.

In general, the present invention contemplates the production of a novel rubberized felted fibrous sheet having physical and chemical properties which render it more suitable for the production of gaskets and other similar purposes than any of the comparable sheet materials which are at present used for such purposes, and to provide a novel and highly efficient and economical method for the production of such fibrous sheet material.

In accordance with the present invention, a mixture of mineral fibers, such as asbestos fibers, glass fibers, rock wool and the like, and a substantial proportion of a curable rubber composition in latex form and which may comprise any of the natural or synthetic rubbers including neoprene, Buna–N, or Buna–S is mixed with water in any usual or preferred form of mixer, including the paper beater. The mineral fibers preferably comprise asbestos fibers within the fiber lengths commercially available under the designations 7–R, 6–D, 5–R and 4–Z. The beating operation is carried out following the general procedure employed in the production of felted fiber board. Uncured rubber is deposited upon and between the mineral fibers by the addition of alum or acid, and after this has been accomplished, the material is sheeted out on any usual or preferred form of paper-making or fibrous-board-making machine and dewatered in the usual manner to form a fibrous sheet. The sheet is then dried to a relatively low moisture content as from 0–2% moisture to enable the sheet to be calendered, but without curing the rubber. The felted fibrous sheet in this condition possesses an appreciable amount of strength and is then calendered to enhance its strength and to impart thereto other desirable properties by causing the uncured rubber particles to flow into intimate association with and to bond together the fiber components. The calendering operation takes place prior to the subsequent curing of the rubber component, and in practice, the curing operation may be effected in a convenient form of tunnel drier at normal rubber-curing temperatures.

In the product produced by the foregoing process, a certain amount of felting of the fibers exists, and the felted structure imparts some tensile strength. The calendering of the sheet having the uncured but curable rubber component interposed between the fibers and deposited thereon causes the uncured rubber to flow into intimate association with the individual fibers and around the same so that upon subsequent curing, the bonding of the fibrous component by the rubber is completed, and there is imparted to the sheet a substantial amount of a rubber feel. The subsequent curing of the material produces a product which possesses superior tensile characteristics and chemical properties which render it particularly suitable for use for the production of gaskets and for other purposes requiring high tensile strength, some flexibility, controlled compressibility, and substantial recovery, as well as the lack of swellability in the fibers when exposed to moisture, and also resistance to water, alcohol, gasoline, and oils encountered in the use of gaskets in the automotive and other industries.

As above stated, the rubber component utilized in the present process may comprise, in latex form, any of the natural rubbers or any of the synthetic rubbers, such as neoprene, Buna–N, or Buna–S together with any of the usual and known curing agents. For the production of gasket material we prefer to utilize neoprene.

	Parts by weight
Asbestos (Canadian 5R)	90
Kraft wood pulp (beaten)	10
Neoprene 735	30
Zinc oxide	4.5
Sulfur	0.6
Agerite white	0.3
Setsit–5	0.9

While the proportion of the rubber component to the fiber component may be widely varied, a lower limit of 10 parts by weight of rubber component to 100 parts by weight of fiber component has been found to be the lower practical limit. The rubber component may be increased up to or appreciably more than the amount of the fiber component, but for practical and economical purposes, most satisfactory results have been obtained using about 25 to 30 parts by weight of rubber component to 100 parts by weight of fiber component.

In the graph illustrated in Fig. 1, tensile strength has been plotted against the neoprene content of a sheet produced in accordance with the present invention wherein the sheet has been calendered to a density of 1.35. The effects of the addition of neoprene in increasing the tensile strength will be apparent from consideration of the graph. The two upper lines indicate the results of test samples taken in the machine direction and the two lower lines of samples taken at right angles to the machine direction.

In Fig. 2, a graph illustrating the compressibility and recovery against the neoprene content illustrates the fact that as the neoprene input increases, the compressibility increases and the recovery decreases. In the graph of Fig. 2, the compressibility is measured as a percentage of the original thickness under a given load, and the recovery is measured as a percentage of the original thickness when the load is removed.

In the graph of Fig. 3 wherein the tensile strength of a 25% neoprene sheet has been plotted against the fiber length of the asbestos, the shorter fiber lengths indicated at 7–R and 6–D as well as the longer fiber lengths indicated at 4–Z appear to impart greater tensile strength than the particular fiber length indicated at 5–R, and these results are reflected in the results of the graph of Fig. 1.

For some purposes where higher or increased tensile

strength is required, we prefer to utilize a minor proportion of a cellulosic fiber with a major portion of mineral fiber, and typical of any of the commercially available cellulosic fibers may be mentioned wood pulp, rags, and any of the other cellulosic fibers available. We prefer to utilize kraft fiber, and experience has demonstrated that by the addition of minor amounts of kraft fiber up to a practical upper limit of kraft fiber of 30% by weight of the total fiber content, the tensile strength has been found to be substantially increased. In the graph illustrated in Fig. 4, a series of curves indicated at A, B, and C have been plotted illustrating tensile strength against the kraft fiber content. The curve A was of a sheet produced using kraft beaten to a freeness of 275 seconds and 25% neoprene; curve B is a similar kraft plus 15% neoprene; and curve C is a kraft beaten to a freeness of 125 seconds freeness and embodying 25% neoprene. The two sets of curves A, B, and C were obtained by test samples in the machine direction and across the machine direction respectively, and from consideration of the curves it will be apparent that the addition of kraft fiber from 5% to 20% unexpectedly increases the tensile strength many fold.

The Rogers test may be briefly described as follows:

Definition

The time necessary for a given quantity of a given consistency of stock solution to drain through a screen at a given temperature.

Apparatus

A 50 mm. glass tube approximately 12 inches long with a 60/40 mesh screen held in position at one end by means of a brass holder so designed as to allow the glass tube to fit into the holder and against the screen. A rubber stopper is placed in the holder to form a watertight cylinder.

Procedure

The consistency of the stock to be tested is determined and a weight equivalent to .9 gram of bone-dry fiber is well suspended in 600 cc. of water at a temperature of 68° F.

This stock solution is poured into the freeness tester and the rubber stopper removed. The time in seconds necessary for the stock solution to drain to a calibrated mark on the tube is taken as the freeness of the stock.

The graph of Fig. 5 illustrates the fact that no advantageous results are obtained beyond a certain freeness in continuing the beating of the fibers beyond that obtained corresponding to from 100 to 275 second freeness.

We have also discovered that the tensile strength and resistance to polar solvents, such as water, the alcohols and ethylene glycol may be substantially increased by the incorporation into the beater with the mineral fiber and rubber components as above described, of a small amount of a "beater addition phenolic resin." Various synthetic resins may be employed comprising alkaline solutions thereof requiring no additional hexa methylene tetramine for curing purposes. This type of resin is the equivalent of a "B-stage" phenolic resin and is known in the art as a "beater addition resin." When diluted with water in the beater, it forms an emulsion, and when subsequently acidified the resin is deposited in particle form on and between the fibers of the stock. Among the beater addition resins obtainable on the market may be mentioned the following:

Bakelite QR 18556
Snyders Synco 730 or 721
Durez 15535

In practice, the proportion of resin is preferably related to the proportion of rubber component, and we have experienced extremely satisfactory results using up to 10% of such a resin in compositions embodying from 25 to 30% of rubber component. If the rubber component is substantially less than 25 to 30%, we prefer to utilize proportionately less resin, and in some instances where the rubber component may run higher than 30% we prefer to increase the resin content. It should be borne in mind that too high a proportion of the resin compound imparts a certain amount of brittleness to the resulting rubberized fibrous sheet. The effect of the addition of a small amount of a "beater addition phenolic resin," such as the phenol formaldehyde sold under the trade name "Synco 730" is, as shown in the graphs of Figs. 6 and 7,

wherein increase in tensile strength is plotted against the resin input in percentages from 1 to 5. It will be observed that small amounts of resin increase the tensile strength extremely rapidly, both in the machine direction and across the machine direction.

In addition to the fact that our research in connection with the development of the present product and the present process had demonstrated that the tensile strength of the felted fibrous sheet is substantially increased both in the machine direction and across the machine direction by the rubber component, and also by the addition of the kraft or other cellulosic fiber component, and also by the addition of a small proportion of the "beater addition phenolic resin," we have also demonstrated that these effects are additive so that with reasonable accuracy one can predict the total increase in tensile strength imparted by both the addition of the kraft and resin from experimental data concerning the effect of each separately.

In Figs. 8 and 9, we have plotted the results of research in connection with the comparison of tensile strength and the density to which the sheet is calendered, and in Fig. 10, we have plotted the compressibility and recovery against the density. From these curves a most unexpected result will be observed, namely, that the weight which a sheet of the present material will support rises rapidly as the density increases. Ordinarily, one would expect the strength per unit weight of a sheet to remain about the same irrespective of density. For example, if any particular strip embodying the invention calendered to a quarter of an inch would support a weight of about 100 lbs., we would normally expect that the same strip squeezed down to about a sixteenth of an inch in thickness would hold about the same weight. Quite unexpectedly, reference to the graph of Fig. 12 shows that as the density increases the tensile strength rises very rapidly, and an increase in density corresponding to curve of the composition indicated, from .8 to 1.3 increases the tensile strength approximately 100%.

From the description thus far, it will be observed that the above-described process of making the rubberized felted fibrous sheet results in the production of a sheet having unusual and unexpected physical and chemical properties which enable the sheet to be used with advantage for the production of gaskets and for other industrial purposes. These unusual properties result from several aspects of the process. The fact that the sheet is calendered before curing of the rubber enables the rubber to flow into intimate association with the felted fibers producing a most efficient bonding effect. The incorporation of the cellulosic fibers within the range specified and the incorporation of the minor proportion of the "beater addition resin" also contribute to imparting most unexpected and desirable characteristics to the product.

Having thus described the invention, what is claimed is:

1. The process of producing a rubberized felted fibrous sheet suitable for gaskets and other purposes, comprising the steps of beating a mixture of mineral fiber and a curable rubber in the form of an uncured latex and precipitating the uncured rubber on the fibers in the form of flowable particles, then sheeting out the fibrous material on a wet machine and dewatering the same to form a fibrous sheet, then drying the sheet sufficiently to enable the sheet to be calendered and without curing the rubber, then calendering the sheet without curing the rubber to impart to the sheet the required density and to cause the uncured rubber to flow around the fibers and into intimate association therewith and thereafter curing the thus calendered sheet by effecting vulcanization of the rubber.

2. The process as defined in claim 1 wherein the drying operation carries the moisture content to approximately 0–2%.

3. The process as defined in claim 1 wherein the drying operation is accomplished by passage of the sheet through a tunnel drier at an air temperature of approximately 350° F. to effect drying of the sheet to a moisture content of from 0–2% and wherein the curing of the sheet is effected by exposure of the calendered sheet to sufficient temperature to cure the rubber.

4. The process of producing a rubberized felted fibrous sheet suitable for gaskets and other purposes comprising the steps of beating a mixture of mineral fiber, a "beater addition phenolic resin," and a curable rubber in the

form of an uncured latex and precipitating the uncured rubber and the phenolic resin on the fibers in the form of flowable particles, then sheeting out the fibrous material on a wet machine and dewatering the same to form a fibrous sheet, then drying the sheet sufficiently to enable the sheet to be calendered and without curing the resin or the rubber, then calendering the sheet without curing the resin or the rubber to impart to the sheet the required density and to cause the uncured rubber and resin to flow around the fibers and into intimate association therewith, thereafter curing the thus calendered sheet by effecting simultaneous curing of the resin and the rubber.

5. A process as defined in claim 1 wherein curable rubber in an amount of from approximately 10 to 50% of the weight of the mineral fiber is incorporated in the beater.

6. A process as defined in claim 1 wherein cellulosic fiber is incorporated in the beater with the mineral fiber in an amount up to 30% of the total fiber content.

7. A process as defined in claim 4 wherein a "beater addition phenolic resin" in an amount of up to 40% of the weight of the rubber is incorporated in the beater with the mineral fiber.

8. A process as defined in claim 4 wherein up to 30% of cellulosic fiber and up to 40% of a "beater addition phenolic resin" based on the weight of the rubber is incorporated in the beater with the mineral fiber.

9. A flexible gasket material consisting of a vulcanized felted rubberized fibrous sheet including mineral fibers in the proportion of from about 80 to 100 parts by weight, and a vulcanizable rubber in the proportion of about 10 to 35 parts by weight.

10. A flexible gasket material comprising, a vulcanized

felted rubberized fibrous sheet consisting of mineral fibers in the proportion of from about 80 to 100 parts by weight; cellulosic fibers in a proportion up to about 20 parts by weight; a vulcanizable rubber in the proportion of about 10 to 35 parts by weight; and "a beater addition" synthetic resin in a proportion up to about 10 parts by weight, the individual mineral and cellulosic fibers being surrounded by cured rubber and vulcanized together and imparting a rubber feel to the sheet.

11. A flexible gasket material comprising a vulcanized felted rubberized fibrous sheet consisting of mineral fibers in the proportion of from about 80 to 100 parts by weight; cellulosic fibers in a proportion up to about 20 parts by weight; a vulcanizable rubber in the proportion of about 10 to 35 parts by weight; and "a beater addition" synthetic resin in a proportion up to about 10 parts by weight, the individual mineral and cellulosic fibers being surrounded by cured rubber and vulcanized together and imparting a rubber feel to the sheet, said gasket material being characterized by densities within the range of from .8 to 1.6 grams per cubic centimeter, and by a variation in tensile strength of from about 1000 to 3000 pounds per square inch when measured in one direction, and from about 2000 to 6000 pounds per square inch when measured in a direction at right angles to said one direction.

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