Sealant composition comprising a fibrillated fiber and a particulate material for automobile cooling system.

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References cited:
US-A-1 429 455
US-A-3 740 337
US-A-3 869 429

SEMINAR NOTES TAPPI, 1981, Nonwoven Fibers & Binders, Atlanta, USA, TAPPI PRESS
E. A. MERRIMAN "KEVLAR® ARAMID PULP FOR PAPER MAKING" pages 5-9

The file contains technical information submitted after the application was filed and not included in this specification

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The present invention relates to a sealant composition for plugging leaks in leaky containers. Particularly, the invention relates to a composition comprising a fibrillated fiber and a particulate material such as a seed meal. The composition of the invention is particularly useful for plugging leaks in heat exchange systems such as automobile cooling systems and the like.

So called "stop leak" compositions have long been used for stopping leaks in automobile cooling systems. Many of these compositions are aqueous suspensions of a particulate material that is entrained in the leak, thereby plugging it. Particulate materials used include linseed meal and metal flake. However these compositions are often not effective in completely stopping the leak, particularly under pressure, resulting in excessive loss of the coolant.

US—A—3,740,337 to Sommer is directed to a stop-leak composition comprising 6 to 9% phenol, 5 to 8% catechu solids, 1.5% to 2.5% sodium metasilicate, 8 to 10% wood fibers (hardwood), 0.3 to 1.0% silicone oil and 72—75% water. This prior composition, wherein the catechu solids function as a coagulant or binder, is so constituted as to congeal only when coming into contact with air.

For many years stop leak compositions were improved by the addition of another fiber to the particulate material. The fibers would in effect fill the voids between the particules plugging the leak, thereby hindering seepage of the leak. However, this was also not always effective and there are now known to be health and environmental problems associated with the use of asbestos. Therefore an improved stop leak composition that is environmentally safe and is more effective in stopping leaks than those heretofore known would be highly desirable.

It has now been found that fibrillated fibers, as defined below, and a particulate material, preferably a seed meal, in combination operate in a synergistic manner to stop leaks more effectively than stop leak compositions of the prior art. The stop leak compositions of the invention are particularly effective under the pressure and temperature conditions found in automobile cooling systems.

The invention in one of its aspects comprises a composition for the stopping of at least one leak in a leaky container which comprises a suspension in a liquid medium of:

(a) swellable particulate material having a size of not less than 0.42 mm and in an amount sufficient to become entrained in the leak, and

(b) fibrillated fiber coating with the particulate material to seal the leak by an entwining action.

In another aspect, the invention comprises a composition as defined above wherein the fibrillated fiber has a length of about 1 mm to about 7 mm and a surface area greater than about 1 m²/g. Preferably the surface area of the fiber is about 10 m²/g.

In another aspect, the invention comprises a method for the plugging of at least one leak in a leaky container which comprises placing in the leaky container a suspension in a liquid medium of swellable particulate material having a size of not less than 0.42 mm and in an amount sufficient to become entrained in the leak and a fibrillated fiber coating with the particulate material to seal the leak by an entwining action.

In another aspect, the invention comprises a method as defined above wherein the fibrillated fiber has a length of about 1 mm to about 7 mm and a surface area greater than about 1 m²/g.

Without being bound to any theory, it is believed that the fibrillated fibers used in the invention provide a bonding of the particulate material as it becomes entrained and begins to form a plug in the leak. As a plug is formed by the particulate material being retained in the leak, the fibrillated fibers interact with these particles by entwining around the particles and providing a bonding together of the particles. Through this interaction a more effective and stronger seal is formed. This differs from prior art compositions that do not contain fibrillated fibers as herein defined, for example asbestos, wherein the fibers do not entwine and bond the particles of the particulate matter. In these prior art compositions the fiber “mats” against the particles in the leak and do not bond or interact with the particles in a synergistic manner, as the fibrillated fibers and particles of the invention. The fibrils used in the prior art essentially provide a mere plugging action of the small leaks between the particles. However in the present invention, the fibrillated fibers not only provide this additional leak plugging but also interact with the particles in a synergistic manner to bond the particles together. This interaction of the particles and the fibrillated fiber is surprising since there is no teaching or recognition in the prior art that fibrillated fibers would co-act with particles differently than any other fiber when used in stop leak composition. The effect of the synergistic interaction resulting from the bonding is a more effective plug than can withstand higher pressures and can plug larger leaks than was generally possible with prior art compositions.

A suitable liquid medium for use in the invention includes any liquid medium in which the fibrillated fiber and particulate matter can be dispersed in effective amounts. Typically the liquid medium comprises water. Also contemplated as liquid media are those containing so called “antifreeze” compositions used in automobile coolent systems. Typically these contain a monohydric or polyhydric alcohol such as methanol or ethylene glycol.

By fibrillated fiber is meant a fiber that is frayed or split along its length or a fiber wherein the ends are split and splayed out, resulting in a multitude of very fine fibrils upon a core fiber. The smaller and thinner fibers or fibrils formed on the core fiber by the fraying or splitting are known as fibrillae. The fibrillated
fibers of the invention can be formed from fibers that are axially oriented and are less strongly bonded in the transverse direction, such as wood, and certain synthetic fibers described below.

A commonly known fiber that can be fibrillated is wood fiber, which can be fibrillated by controlling the cutting conditions of the fiber. The fibrillating of wood fiber is explained by Julino Grant in Laboratory Handbook of Pulp and Paper Manufacture, 2nd Edition, 1961, Great Britain, at pp. 147—152.

Fibrillated fibers made from synthetic materials are also contemplated for use in the invention. Examples of synthetic fibrillated fibers and methods for making them are disclosed in United States Patent 3,097,991, issued to W. A. Miller et al. on July 16, 1963 and United States Patent 3,560,318, issued to W. A. Miller, et al. on February 2, 1971. Processes for making synthetic fibrillated fibers typically involve the cutting and beating of a fiber or a film of an oriented polymer, in for example a paper beater. Synthetic polymers can be formed into oriented films or fibers by methods known in the art. These typically involve the controlling of the extrusion process and/or a stretching process to orient the polymer in the film or fiber. The oriented fibers or films must be stronger in an axial direction and weaker in a transverse direction to an extent to allow fibrillation. Optionally the polymer can be coextruded with an incompatible polymer, as is described in the above cited patents, to more readily form a fiber or film that is strong in an axial direction and weak in a transverse direction. This can be accomplished by addition of the incompatible polymer to the polymer melt or the polymer solution or “dope” that is to be extruded. Some polymers such as poly(1,4-phenyleneiminoterephthalamide), described below, may be formed in a highly oriented state with long, strong, axia, crystalline “grains” separated by weaker amorphous regions, and may not require the use of an incompatible polymer to form fibrillatable fibers. The formation of fibrillated fibers from synthetic polymers is well known in the art.

The fibrillated fibers used in the invention should be fibrillated to the extent to provide the synergistic coaction of the invention. This includes fibrillated fibers having a surface area greater than about 1 m²/g. Preferably the surface area is about 10 m²/g. The surface area of the fiber is measured by the B—E—T method as described by Brunauer, et al. in J. Am. Chem. Soc., 60, 309 (1938).

The length of the fibrillated fiber should be great enough to provide the entwining coaction with the particles used in the invention. This includes fiber having an average length greater than or equal to 1 mm. The fibrillated fiber should not be too long to interfere or hinder the fluid flow within leaky containers such as within automobile cooling systems where such fluid flow is desirable. In the typical practice of the invention, the average length of the fibrillated fiber is about 1 mm to about 7 mm.

The fibrillated fibers of the invention must be of a substance that is stable. By stable is meant a substance that doesn’t significantly react or degrade in the environmental conditions in which the composition of the invention is used. For use in automobile cooling systems and the like, this would be a substance that is thermally stable up to about 149°C (300°F), preferably up to about 260°C (500°F), and is unreactive with the components of the coolant, such as water, corrosion inhibitors, anti-freeze compositions and other substances commonly found in automobile cooling systems.

Any polymers that can be made into a fibrillated fiber is suitable for use in the fibrillated fibers of the invention. Suitable polymers include the polyamides and the polysulfones. The preferred fiber for use in the invention is a fiber comprising a polymer consisting essentially of the recurring units selected from the group;

\[
\begin{align*}
&\text{(I)} \\
&\quad \text{O} \\
&\quad \text{C—R"—C—} \\
&\text{(II)} \\
&\quad \text{H} \\
&\quad \text{N—R'—N—} \\
&\text{(III)} \\
&\quad \text{O} \\
&\quad \text{C—R"—N—}
\end{align*}
\]

with the proviso that

\[
\begin{align*}
&\quad \text{O} \\
&\quad \text{C—} \\
&\text{and} \\
&\quad \text{H} \\
&\quad \text{N—}
\end{align*}
\]

are present in the polymer in substantially equimolar amounts, and wherein R, R' and R" may be
same or different, are divalent radicals, n may be zero or the integer one, and wherein the R, R', and R'' radicals in the polymer are saturated or unsaturated aliphatic or ringed aliphatic radicals containing 1 to 10 carbon atoms, or single ringed or fused multiringed carbocyclic or heterocyclic aromatic radicals. The R, R', or R'' may contain substituents and other radicals that do not unduly interfere with the ability to form fibrillated fibers, for example through cross-linking, or cause the fiber to become too unstable to too chemically reactive for practice of the invention. The preferred polymers of the class, described above for use in the fibrillated fibers of the invention are those where the R, R', and R'' in the polymer are single rigid radicals with extended bonds or a series of such rigid radicals which are linked together directly by extended bonds. Thus, the essential portion of the polymer consists of polyamide units (including polyoxamide units when n is zero), which provide stiff chains.

By the expression “rigid radicals” is meant (a) the ring radicals: single ring or fused multi-ring aromatic carbocyclic or heterocyclic radicals, trans-1,4-cyclohexylene

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

and 1,4(2,2,2)bicyclo-octylene and (b) the linear unsaturated radicals: vinylene

\[
\text{H} \quad \text{H}
\]

and acetylene—C=CC—. It will be understood that monomers containing amino groups directly attached to linear unsaturated radicals are not stable and hence vinylene or acetylene cannot serve as R' or that portion of a R'' radical attached to

\[
\text{H} \\
\text{N}
\]

By the expression “extended bonds” is meant chain-extending bonds of the radical (as determined by the true bond angles) which are essentially coaxial or parallel and oppositely directed, such as in p-phenylene and 1,6-naphthylene.

A more preferred class of polymers of the group described above are those polyamides (n being the integer one) wherein at least 50 mole percent of the total of R, R', and R'' radicals are wholly aromatic. A more preferred class of these polymers are those polyamides wherein R, and R' are selected from the group 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthylene, 2,5-pyridene, trans-vinylene and trans-1,4-cyclohexylene and R'' is 1,4-phenylene with the proviso that at least 50 mole percent of either R or R' radicals are 1,4-phenylene.


The most preferred fiber consists essentially of poly(4-methyleneiminoterephthaloyl) which is a polyamide polymer characterized by the repeating unit,

\[
\begin{align*}
\text{N} & \quad \text{H} \\
\text{H} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\end{align*}
\]

This polymer is available commercially as Kevlar (trademark) from E. I. duPont de Nemours & Co., Centre Road Building, Wilmington, Delaware, in a “pulp” form. This “pulp” consists essentially of short fibrillated fibers or fibers with a multitude of fibrillae or very fine fibrils upon a core fiber. Kevlar (trademark) pulp is described by Merriman in “Kevlar (trademark) Arimid Pulp for Paper Making”, reprinted from 1981 TAPPI Non-Woven Fibers and Binders Seminar Notes, TAPPI 1981. The method for forming fibrillated fibers of this polymer is not disclosed, but these fibrillated fibers are probably formed in a manner similar to the well known methods, discussed above, for forming fibrillated fibers from synthetic materials. These fibers are most preferred in the composition of the invention because of their fibrillations, high thermal stability and inertness to chemical and biological action.
As used herein, the term "particulate material" means any material comprising particles that when used in the composition and method of the invention become entrained in the leak. Particulate materials useful in the invention include any particulate material wherein the particles thereof retain their physical integrity in the environment in which it is used. Preferably the particulate material has a density near that of the liquid medium in which it is suspended. Without being bound to any theory, it is believed that the effective particulate materials are those that are swellable under cooling system conditions to form a plug in the leakage opening that is more firm and resists pressure better than would be the case if swellable particulate material was not used. By "swellable" particulate material is meant those organic materials that absorb water to form a soft exterior but retain their physical integrity. These include hard organic particulate materials that when placed in water will form a particulate with a soft exterior but retain a hard interior. Examples include seed meals, ground roots, cellulosic materials such as wood and the like.

The preferred particulate material is seed meal. The seed meal for use in the invention includes the meals from which the oil has been extracted and are usually byproducts of processes for extracting seed oil, such as solvent extraction and presses. The meal of any seed should be suitable. Suitable seed meals include linseed meal, joboza bean meal, and soybean meal. The preferred seed meal is soybean meal.

The composition of the invention is made by dispersing the fibrillated fiber and the particulate material in a liquid medium. This may be accomplished by any suitable method. An additive, such as a dispersant, may be necessary to disperse the fibrillated fiber. The choice of a dispersant is not critical and can include surfactants common in the art or those substances that have the same properties. Suitable surfactants include the quaternary ammonium compositions used as surfactants, such as quaternary ammonium chloride.

It is preferably that a suspending agent be used to prevent settling of the seed meal. Suitable suspending agents include various alumino-silicate clays that are known in the art as suspending agents, such as the bentonite-type clays. Suitable clays for suspending agents include Bentonite GPG—30 and HPM—20 manufactured by American Colloid Co., Skokie, Illinois, and available from Whittaker, Clark & Daniels, Inc., 1000 Coolidge Drive, South Plainfield, New Jersey. A preferred clay is a bentonite clay such as Bentonite GPG—30. The suspending agent may also aid in the dispersion of the fiber, rendering unnecessary the use of a surfactant.

A thickener may additionally be used to hinder settling of the components, particularly the particulate material. Other additives may be desirable such as buffering agents. Addition of a preservative to prevent biological degradation and fermentation of the seed meal is preferred. It may also be desirable to add a "drier". A drier is generally an alumino-silicate clay that has the function of drying a very slow or seeping leak.

Other optional additives may be employed. These include, for example, known corrosion inhibitors used to protect surfaces of aluminum, iron and other metals or materials that may be used as a material of construction of the leaky container or other surface that may contact the liquid medium. The corrosion inhibitors include silicone-stabilized silicone/silicate copolymer corrosion inhibitors, molybdates, alkanolamine salts of silicates, borates, phosphates, benzoates hydroxy benzoates or acids thereof, silicenes, alkali metal nitrates alkali metal nitrates, tolytriazole, alkali metal or alkanolamine salts of silicates, mercaptobenzothiazole and the like, or mixtures thereof. If one or more of the known inhibitors are employed, the sum total of all inhibitors should be used in an "inhibitory effective amount", i.e., an amount sufficient to provide some corrosion inhibition with respect to the surfaces to be protected. Other typical optional additives would include wetting agents and surfactants such as, for example, known ionic and non-ionic surfactants such as the poly (oxyalkylene) adducts of fatty alcohols; antifoams, and/or lubricants such as the well-known polysiloxanes and the polyoxyalkylene glycols, as well as any other minor ingredients known in the art that do not adversely affect the corrosion resistance sought to be achieved. In a preferred method of the invention, the fibrillated fiber and the particulate matter is dispersed in a liquid medium to form a suspension which is a composition of the invention. The suspension is then added to the leaky container, preferably an automobile cooling system, containing a liquid coolant. The suspension is then diluted and dispersed in the container to form a second suspension, also a composition of the invention. In an automobile cooling system the dispersion is provided automatically by the flow of the coolant in the system as it operates. The second suspension then provides effective amounts of fibrillated fiber and particulate matter to seal leaks.

The composition of the invention contains sufficient fibrillated fiber and swellable particulate matter to provide a synergistic leak stopping ability. The effective amounts of the fibrillated fiber and swellable particulate matter vary widely and depend upon the nature and size of the leak, the environmental conditions of the leaky container and the particulate fiber and particulate material used. The effective amount of the swellable particulate material is that amount required for particles to become entrained in the leak as the fluid flows therethrough. The effective amount of fibrillated fiber is that amount necessary to interact in the above described manner with the particulate material that is entrained in the leak. It has been found that as long as some particulate material becomes entrained in the leak only a very small amount of fibrillated fiber is necessary to interact with the particulate material to provide the synergistic results of the invention. In tests of compositions of the invention similar to those recited in the examples below, it was found that a significant proportion of the fibrillated fiber remained free in
suspension after leaks were completely sealed. This would indicate that there was an excess of fiber in these compositions and that the minimum effective amount of fibrillated fiber would be significantly less than that found in these compositions. Generally contemplated in the invention for commercial and practical reasons relating, for example to ease formulation, are compositions containing fibrillated fiber and swellable particulate material at a weight ratio of about 1:20 to about 20:1, preferably about 1:5 to about 1:15, most preferably about 1:10 of fibrillated fiber to swellable particulate matter. However, as indicated above, a smaller proportion of fibrillated fiber is probably effective in stopping leaks.

The size of the leak the composition of the invention will effectively seal is dependent upon the size of the particles of the particulate material and the type of particulate material used. Generally the size of the particles in the swellable particulate material should be such that under the environmental conditions of the leaky container, particles become entrained in the leak. Particles approximately near the size of the leak and larger are generally suitable, although it should be considered that in the environment found in the leaky container, such as the higher pressures and temperatures found in automobile cooling systems, the particles may swell or otherwise change in volume. Generally it is desirable to avoid a large proportion of very fine particles (under about 0.42 mm or 35 mesh Tyler in a dry condition) in the particulate material. For use in automobile cooling systems the particulate material is preferably soybean meal between about 0.42 mm (35 mesh Tyler) and about 0.70 mm (24 mesh Tyler). To seal a crevice leak of about 0.457 mm (0.108 inch) or less, a soybean meal that passes through a 0.84 mm (20 mesh Tyler) screen when dry was found suitable in plug leaks under conditions typifying an automobile cooling system (about 77°C or 170°F to about 121°C or 250°F and up to about 1.03 x 10⁶ Pa above atmospheric pressure or 15 psig). A composition of the invention containing soybean meal screened through an 0.84 mm (20 mesh Tyler) screen when dry was found to seal crevice leaks as large as 0.508 mm (0.020 inches) under similar conditions.

The following examples illustrate the invention and compare it with prior art compositions. They are not intended to limit the invention in any way.

Example 1

A stop leak composition of the invention is made by dispersing in tap water a fibrillated fiber and soybean meal. To disperse the fibrillated fiber and suspend the soybean meal an alumino-silicate clay (Bentonite GPG—30 from American Colloid Co., Skokie, Ill.) is used. Borax is used as a buffer. Additionally a preservative (UCARIDE (trademark) available from Union Carbide Corporation, Old Ridgebury Road, Danbury, Connecticut), a seeping leak dryer (Attack available from A. E. Fleming, 13315 Stephen Road, Warren, Michigan) and a thickener (ASE—6 available from Rohm & Haas, Independence Mall West, Philadelphia, Pa.) are added.

The fibrillated fiber is Kevlar (trademark) 29 Aramid Pulp and is generally described above as the most preferred fiber. The pulp is designated Merge 6F218, has fiber lengths in the range of about 1 mm to about 4 mm with a nominal average length of about 2 mm and has a surface area of about 10 m²/g.

The soybean meal is obtained from Cargill, Incorporated, 2400 Industrial Drive, Sidney Ohio, and has the analysis, in weight percent of the meal, as shown in Table I. The soybean meal is ground and screened while dry through a 0.70 mm (24 mesh Tyler) screen.

| TABLE I |
|-------------------|-----------|
| Crude Protein     | ≥ 4.4%    |
| Crude Fat         | ≥ 0.50%   |
| Crude Fiber       | ≤ 7.0%    |
| Ash               | ≤ 7.0%    |
| Moisture          | ≤ 12.0%   |

The amounts of the components are not critical, however, for a commercial formulation of a stop leak composition of the invention, suitable amounts of the components in weight percent based on the total weight of the composition are as follows: about 4 to about 7, preferably about 5 to 7 percent of the suspending agent; about 0.5 percent of the borax; about 0.6 to about 1 percent of the preservative; about 1 to about 5, preferably about 1 to about 3 percent of the soybean meal; about 0.1 to about 0.5, preferably about 0.1 to about 0.3 percent of the fibrillated fiber; about 1 percent of the dryer; and about 0.5 to about 0.8 percent of the thickener; with water constituting the remainder of the composition. The above recited ranges are for a composition that is to be used in an automobile cooling system and is to be added to and diluted by the coolant liquid according to the preferred method of the invention recited above. The dilution ratio contemplated for the composition of this example is about 3.2 parts composition to about 100 parts of the combined stop leak composition and coolant. This corresponds to the addition of about a 0.5 litre 16 fluid ounce can of stop leak composition to a 15 litre (16 quart) cooling system.
Example 2

Compositions made according to the invention, containing a swellable particulate material and a fibrillated fiber, were tested. For comparison, compositions using a nonfibrillated fiber (asbestos fiber) and a seed meal were also made and tested.

A bench test unit was used to measure the effectiveness of the compositions tested. The bench test unit was made with pressure and temperature conditions typically found in an automobile cooling system. It comprised a vertical closed cylindrical reservoir 98.4 mm (3 3/4 inches) in diameter and 139.7 mm (5 1/2 inches) high fitted with a flanged leakage adapter 38.1 mm (1 1/2 inches) from the reservoir bottom, and a pressure fitting above the fluid line in the reservoir. The pressure fitting was attached to a pressure regulated compressed air source such that any desired pressure in the reservoir could be achieved. The reservoir was also fitted with a thermoregulator (Fenwal-Thermoswitch, size no. 17100 115V, Scientific Glass and Apparatus Co.); and a heater (Chromaloy RI—250 115V, 250W). Attached to the reservoir was an inlet and outlet for circulating liquid using an external pump. The inlet was a 9.5 mm (5/16 inch) brass tube and was located about 38 mm (1 1/2 inches) from the reservoir bottom. This tube was curved at a 45 degree angle to divert the inlet stream from the leak opening and to give the liquid a clockwise swirling motion. Also provided were a pressure gauge and a bimetallic type thermometer. The fluid capacity of the entire system was about 0.3 liters. The leakage adapter was 60.3 mm (2 3/4 inches) in diameter with a 19.0 mm (5/8 inch) high base and had a 12.7 mm (1/2 inch) deep threaded fitting for attachment to the reservoir. To the base was bolted a 60.3 mm (2 3/4 inch) diameter plate of non-magnetic stainless steel in the 300 series which contained the required hole or leak. The plate consisted of two abutting 6.35 mm (1/4 inch) thick sections with a notch cut into one section to provide the leak. The leak was a centered crevice and was 12.7 mm (0.5 inch) long and 0.457 mm (0.018 inch) wide. A crevice leak stopping abilities of more effectively tests leak stopping abilities of the stop leak compositions than a "pin-hole" leak, which can be plugged with a single particle. A catch pot was provided to catch leaking liquid.

Before each test, the test unit was cleaned by disassembly of the unit, mechanically removing any stop leak material and flushing the unit by pumping through it a rinse solution of water and detergent. The flushing is repeated until the unit is free of all stop leak material.

The tests were accomplished by adding 29 ml of the stop leak composition to water to give a liquid total 900 ml which was added into the test unit, which was then closed. The pump was started and the temperature of the fluid was raised to 87.8 ± 3°C (190°F ± 5°F). The fluid flow rate was set at about 1,100 grams/min. The unit was so operated with no pressure for 5 minutes after which the pressure was slowly built up to 1.03 x 10^8 Pa above atmospheric pressure (15 psig) over a period of 2 1/2 minutes by incrementally increasing the pressure by 0.17 x 10^5 Pa (2 psig) every 30 seconds and then holding the pressure at 1.03 x 10^8 Pa above atmospheric pressure (15 psig) for 5 minutes. The volume of the fluid lost after the leak was sealed and the nature of the leak were noted.

Compositions using a fibrillated fiber useful in the invention and soybean meal were made and compared with compositions of the fiber alone and the soybean meal alone. The fibrillated fiber and the soybean meal are the same as those described in Example 1. The fiber was dispersed in water with Bentonite GPG—30 clay, which was also used as a suspender. The clay was used in an amount of 5 weight percent based on the total weight of the composition. After the fiber was dispersed the seed meal was added and dispersed. The total of the fibrillated fiber and the seed meal in the stop leak composition was set at 1.50 weight percent, based on the total weight of the composition. A summary of the tests is shown in Table II.

<table>
<thead>
<tr>
<th>Wt. % Stop Leak Component</th>
<th>Vol. Fluid Lost</th>
<th>Nature of Leak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean Meal</td>
<td>Fibrillated Fiber</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>None</td>
<td>75 ml, Dripping at end of test.</td>
</tr>
<tr>
<td>1.23</td>
<td>0.27</td>
<td>54 ml, sealed</td>
</tr>
<tr>
<td>0.75</td>
<td>0.75</td>
<td>47 ml, sealed</td>
</tr>
<tr>
<td>0.27</td>
<td>1.23</td>
<td>10 ml; sealed</td>
</tr>
<tr>
<td>None</td>
<td>1.50</td>
<td>all fluid lost, no seal.</td>
</tr>
</tbody>
</table>

The above results show the synergistic effect of using both the fibrillated fiber and the seed meal. Comparative tests were run with compositions of soybean meal and asbestos fiber and each alone.
These tests were run essentially as above except instead of the fibrillated fiber an asbestos fiber was used. The asbestos fiber was from Johns Manville Corp., Englewood Cliffs, New Jersey, and coded 7T05. A summary of these tests is in Table III.

<table>
<thead>
<tr>
<th>Wt. % Stop Leak Component</th>
<th>Vol. Fluid Lost Nature of Leak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean Meal</td>
<td>Asbestos Fiber</td>
</tr>
<tr>
<td>1.50</td>
<td>None</td>
</tr>
<tr>
<td>1.23</td>
<td>0.27</td>
</tr>
<tr>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>0.27</td>
<td>1.23</td>
</tr>
<tr>
<td>None</td>
<td>1.50</td>
</tr>
</tbody>
</table>

As shown by the above results, asbestos containing compositions of the prior art do not show the synergistic effect of the invention and are substantially inferior in leak stopping ability than the compositions of the invention. The asbestos fiber compositions of the prior art allowed a significantly larger amount of leakage, nearly an order of magnitude larger, than the compositions of the invention. In the test of the asbestos fiber containing compositions there were not a complete seal and if the test were sufficiently long a complete loss of fluid would have resulted. However, in the tests of the compositions made according to the invention, a complete seal was achieved and no further leakage would have occurred. The results demonstrate the synergistic action of the particles and the fibrillated fiber used in the invention in inhibiting fluid loss and achieving a complete seal of the leak.

As an alternate embodiment, the above described compositions may contain a corrosion inhibitor in an inhibitory effective amount, such as those described above and those known in the art. Corrosion inhibitors are well known and are disclosed in several patents, such as, for example, United States Patent 3,198,820, issued August 3, 1965 to Pines and United States Patent 3,337,496, issued August 22, 1967 to Snyder et al.

**Claims**

1. A composition for the stopping of at least one leak in a leaky container which comprises a suspension in a liquid medium of:
   (a) swellable particulate material having a size of not less than 0.42 mm and in an amount sufficient to become entrained in the leak, and
   (b) fibrillated fiber coacting with the particulate material to seal the leak by an entwining action, preferably said composition containing at least a corrosion inhibitor in an inhibiting effective amount.

2. The composition of claim 1 wherein the fibrillated fiber has a length of about 1 mm to about 7 mm and a surface area greater than about 1 m²/g.

3. The composition of Claim 1 or 2 wherein the fibrillated fiber comprises a polymer consisting essentially of the recurring units selected from the group:

   - O
   - O
   - C – R – C
   - H
   - H
   - N – R’ – N
   - O
   - H
   - C – R” – N

   with the proviso that
are present in the polymer in substantially equimolar amounts, and wherein R, R', and R'', which may be the same or different, are divalent radicals, n may be zero or the integer one, and wherein the R, R', and R'' radicals in the polymer are saturated or unsaturated aliphatic or ring aliphatic radicals containing 1 to 10 carbon atoms, or single or fused multiringed carbocyclic or heterocyclic aromatic ringed radicals or a series of such radicals, preferably wherein n is the integer one and wherein R, and R' are selected from the group 1,4-phenylene, 4,4'-biphenylene, 2,6-naphtylene, 2,5-pyridene, trans-vinylene and trans-1,4-cyclohexylene and R'' is 1,4-phenylene with the proviso that at least 50 mole percent of either R or R' radicals are 1,4-phenylene and more preferably wherein the polymer consists essentially of the repeating unit

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

4. The composition of Claim 1 or 2 wherein the swellable particulate material is a seed meal, preferably soybean meal.
5. The composition of claim 1 or 2 wherein the liquid medium comprises a monohydric or polyhydric alcohol, preferably ethylene glycol.
6. The composition of claim 1 or 2 wherein the liquid medium comprises water.
7. The composition of claim 1 or 2 having a weight ratio of fibrillated fiber to swellable particulate material of about 1:20 to about 20:1 preferably from about 1:5 about 1:15 and more preferably about 1:10.
8. A method for the plugging of at least one leak in a leaky container which comprises using a composition as claimed in anyone of the claims 1 to 7.

**Patentansprüche**

40. 1. Zusammensetzung für das Unterbinden mindestens einer Leckstelle in einem leckenden Behälter, aufweisend eine Suspension in einem flüssigen Medium von:
(a) einem quellbaren Partikelmaterial mit einer Größe von nicht weniger als 0,42 mm und in einer ausreichenden Menge, um in das Leck mitgeführt zu werden, und
(b) mit dem Partikelmaterial zusammenwirkenden fibrillierten Fasern, um das Leck durch einen Verflüssigungsvorgang zu verschließen, wobei die Zusammensetzung vorzugsweise wenigstens einen Korrosionsinhibitor in einer korrosionshemmend wirksamen Menge enthält.
7. Zusammensetzung nach Anspruch 1, in der die fibrillierten Fasern eine Länge von ungefähr 1 mm bis ungefähr 7 mm und eine spezifische Oberfläche von mehr als ungefähr 1 m²/g aufweisen.
5. Zusammensetzung nach Anspruch 1 oder 2, in der die fibrillierten Fasern ein Polymer aufweisen, welches in wesentlichen aus sich wiederholenden Bausteinen, ausgewählt aus der Gruppe

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{C} \cdots \text{C}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \cdots \text{N}
\end{array}
\]

besteht, mit der Maßgabe, daß
in dem Polymer in im wesentlichen äquimolaren Mengen zugegen sind, und worin R, R' und R'' die gleich oder unterschiedlich sein können, zweiseitig sind, n gleich null oder ganzzahlig eins sein kann, und worin R—, R'— und R''— im Polymer gesättigte oder ungesättigte aliphatische oder zyklisch-aliphatische Gruppen mit 1 bis 10 Kohlenstoffatomen sind, oder einzelne oder verkettete mehrringige carbocyclische oder heterocyclische aromatische Ring-Gruppen oder eine Folge solcher Gruppen, vorzugsweise solche, in denen n ganzzahlig gleich eins ist, und in denen R und R' aus der Gruppe 1,4-Phenylen, 4,4'-Biphenylen, 2,6-Naphthylen, 2,5-Pyriden, trans-Vinylend und trans-1,4-Cyclohexylen ausgewählt sind und R'' 1,4-Phenylen ist, mit der Maßgabe, daß mindestens 50 mol% entweder von R oder R' 1,4-Phenylen sind, und worin besonders bevorzugt das Polymer im wesentlichen aus dem sich wiederholenden Baustein

besteht.

4. Zusammensetzung nach Anspruch 1 oder 2, in der das quellbare Partikelmaterial ein grobes Semenmehl, vorzugsweise Sojabohnenmehl ist.

5. Zusammensetzung nach Anspruch 1 oder 2, in der das flüssige Medium einen einwertigen oder zweiwertigen Alkohl, vorzugsweise Ethyenglykol aufweist.

6. Zusammensetzung nach Anspruch 1 oder 2, in der das flüssige Medium Wasser aufweist.


8. Verfahren zum Verstopfen mindestens eines Lecks in einem leckenden Behälter, welches die Verwendung einer Zusammensetzung nach irgendeinem der Ansprüche 1—7 einschließt.

**Revendications**

1. Composition permettant de boucher au moins une fuite dans un reservoir qui fuit, qui comprend une suspension dans un milieu liquide:
   (a) d'une matière susceptible de gonfler, formée de particules ayant un diamètre non inférieur à 0,42 mm, et en une quantité suffisante pour être entraînée vers la fuite, et
   (b) de fibres fibrillées agissant conjointement avec la matière en particules pour obturer la fuite par une action d'entrelacement, ladite composition contenant de préférence au moins un inhibiteur de corrosion en une quantité à effet inhibiteur.

2. Composition suivant la revendication 1, dans laquelle les fibres fibrillées ont une longueur d'environ 1 mm à environ 7 mm et une surface spécifique supérieure à environ 1 m²/g.

3. Composition suivant la revendication 1 ou 2, dans laquelle les fibres fibrillées sont formées d'un polymère comprenant essentiellement des motifs répétés choisis dans le groupe:
sous réserve que

soient présents dans le polymère en des quantités pratiquement équimolaires, motifs dans lesquels $R$, $R'$ et $R''$, qui peuvent être identiques ou différents, sont des radicaux divalents, $n$ peut être égal à zéro ou au nombre entier un et les radicaux $R$, $R'$ et $R''$ sont des radicaux aliphatiques ou cycloaliphatiques saturés ou insaturés contenant 1 à 10 atomes de carbone ou des radicaux aromatiques carbocycliques ou hétérocycliques à un seul cycle ou à plusieurs cycles condensés, ou bien une série de ces radicaux, $n$ étant de préférence le nombre entier un, $R$ et $R'$ étant choisis entre les radicaux, 1,4- phényléne, 4,4'-biphényléne, 2,6-naphthylène, 2,5-pyridène, trans-vinylène et trans-1,4-cyclohexylène et $R''$ étant le radical 1,4-phényléne, sous réserve qu’au moins 50 moles pour cent des radicaux $R$ et $R$ soient des radicaux 1,4-phényléne, le polymère comprenant de préférence essentiellement le motif répété

![Chemical structure](image)

4. Composition suivant la revendication 1 ou 2, dans laquelle la matière en particules susceptible de gonfler est une farine de graine, de préférence de la farine de soja.

5. Composition suivant la revendication 1 ou 2, dans laquelle le milieu liquide comprend un alcool monohydroxylique ou polyhydroxylique, de préférence l'éthyléneglycol.

6. Composition suivant la revendication 1 ou 2, dans laquelle le milieu liquide renferme de l'eau.

7. Composition suivant la revendication 1 ou 2, qui possède un rapport pondéral des fibres fibrillées à la matière en particules susceptible de gonfler compris dans l'intervalle d'environ 1:20 à environ 20:1, de préférence d'environ 1:5 à environ 1:15 et notamment égal à environ 1:10.

8. Procédé pour boucher au moins une fuite dans un réservoir qui fuit, qui consiste à utiliser une composition suivant l'une quelconque des revendications 1 à 7.