Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

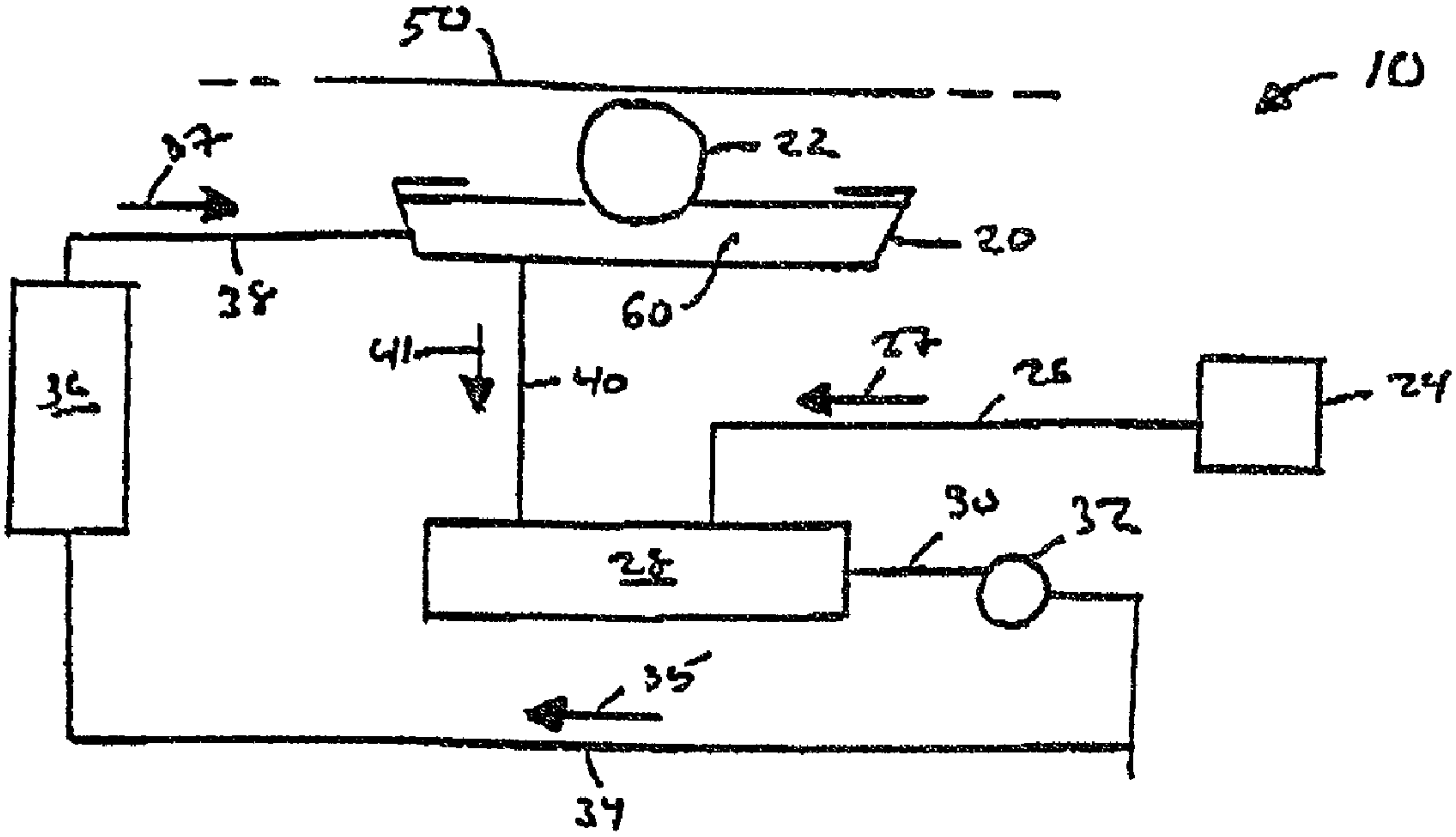
Canadian Intellectual Property Office
An agency of Industry Canada

CA 2057461 C 2004/07/13
(11)(21) 2 057 461
(12) BREVET CANADIEN
CANADIAN PATENT
(13) C

(22) **Date de dépôt/Filing Date**: 1991/12/10
(41) **Mise à la disp. pub./Open to Public Insp.**: 1992/10/27
(45) **Date de délivrance/Issue Date**: 2004/07/13
(30) **Priorité/Priority**: 1991/04/26 (07/692,304) US

(51) **Cl.Int.^{5}/Int.Cl.^{5}** E04D 1/12, C08K 5/01, C08L 95/00
(72) **Inventeurs/Inventors**:
TERRENZIO, LOUIS A., US;
NOONE, MICHAEL J., US
(73) **Propriétaire/Owner**:
CERTAINTEED CORPORATION, US
(74) **Agent**: SMART & BIGGAR

(54) **Titre** : BARDEAU
(54) **Title**: SHINGLE



(57) **Abrégé/Abstract**:
An improved sealant composition for asphalt shingles includes a blown asphalt having a softening point of from about 180°F to 230°F and a mixture of at least two thermoplastic elastomers, the thermoplastic elastomer being from about 5 to 15 percent by weight of the sealant.

2057461

ABSTRACT

An improved sealant composition for asphalt shingles includes a blown asphalt having a softening point of from about 180°F to 230°F and a mixture of at least two thermoplastic elastomers, the thermoplastic elastomer being from about 5 to 15 percent by weight of the sealant.

SHINGLE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to bituminous roofing membranes or shingles, and more particularly to sealants for holding asphalt shingles in place on roofs.

2. Brief Description of the Prior Art

Asphalt roofing shingles are often manufactured with an intermittent strip or bead of bituminous sealant applied longitudinally across the face of the shingle, just above or in back of the portion of the shingle forming the tabs. This sealant bead is often covered with a strip of release paper when the shingle is manufactured. The shingles are then stacked, and the stacked shingles packaged for shipment. On the job site, the shingles are applied one at a time to the roof, with the release paper strips being removed from the shingles in each course as that course of shingles is fastened to the roof, just before the next course is added. The next course is positioned and fastened so that the tabs of shingles in the next succeeding course over lie, and stick to, the sealant beads of the shingles in the course underneath. The sealant is intended to help hold down roofing shingles which are exposed to adverse environmental conditions, such as high winds.

When the sealant beads are covered with release paper, they may be formed using a sealant composition which is tacky at ambient temperatures, as the release paper is intended to prevent premature adhesion of individual shingles when the shingles are stacked during shipment and storage. In this case, the sealant composition can be formulated, using a very soft grade of a bitumenous material, such as "roofer's flux," a very soft asphalt. This type of sealant composition is exemplified in U.S. Patent No. 4,559,267.

On the other hand, if a release paper is not employed, the sealant composition must not be tacky at ambient temperatures, and a harder bituminous material must be used, so that the shingles do not stick together in the stack. In this case, the sealant composition can be formulated to become tacky at a temperature above that expected to be encountered during storage of the stacked shingles, but below which it can be expected the installed shingles will attain, such as when exposed to full sun. For example, the sealant composition in this case can be formulated to become tacky at a temperature of from about 140°F to

150°F.

Both types of prior art sealant compositions have disadvantages. For example, sealants which are tacky at ambient temperatures may experience excessive "cold flow" so that the sealant bead is squashed down or flattened during storage of the stacked shingles. This may cause the sealant to seep out from under the release paper, and cause the stacked shingles to inadvertantly adhere to one another before installation. Further, if the sealant bead is spread out too much, it may not then extend far enough above the mineral granules on the shingle face to provide a good bond with the undersides of the tabs of the overlying shingles when the shingles are applied to the roof. Similarly, if the bead is not adhesive at ambient temperatures, it may become adhesive unintentionally before the shingles are installed on a roof, causing the stacked shingles to adhere to one another. For example, the stacked shingles may be accidentially stored in full sun, or in too warm a warehouse. Even if the stacked shingles are stored at a relatively low temperature, the sealant composition may still "cold flow" over time to give the undesired adhesion. Further, the relatively hard grades of bituminous materials employed in preparing this type of sealant composition can exhibit poor low temperature properties, and become hard and brittle at ambient temperatures such as those encountered by the installed shingles during winter months. Poor low temperature properties may be reflected in cracking of the sealant bead, loss of adhesion, or the like.

There is a need for a sealant composition which resists cold flow and "squash out" during storage of the stacked shingles to which it has been applied, yet which also provides gool adhesion for the shingles installed on a roof, while simultaneously showing good flexibility and adhesion at low temperatures.

SUMMARY OF THE INVENTION

The present invention provides an improved sealant composition for a bituminous roofing membrane and an improved shingle, including a sealant strip or bead formed from the improved sealant composition. The improved sealant composition exhibits improved cold flow or "squash out" resistance, and good low temperature performance properties, and the improved shingle can be stored in stacks without loss of adhesion when the shingles are installed on a roof.

The improved sealant composition of the present invention includes a bituminous material, preferably a blown asphalt, having a softening point of from about

180°F to 220°F, more preferable from about 195°F to 205°F, with a softening point of about 199°F being especially preferred. In addition, the improved sealant composition includes a rubbery material, preferably the rubbery material being thermoplastic elastomer, with a mixture of two thermoplastic elastomers, such as a mixture having different average particle sizes, being more preferred. The rubbery material can comprise from about five to fifteen percent by weight of the improved sealant composition. Preferably, the rubbery material comprises from about ten to twelve percent by weight of the improved sealant composition.

The rubbery material is advantageously formulated in a pre-blend with at least one resin or plasticizer selected to enhance the compatibility and dispersibility of the rubbery material in the bituminous material. In addition, the pre-blend, or additive composition can include other components, such as antioxidants, ultraviolet light stabilizers, solvents, and the like. Preferably, the rubbery material is thermoplastic elastomer and comprises from about 30 to 70 percent by weight of the pre-blend composition. Preferably, the rubbery material is a styrenic thermoplastic elastomer, such as a styrene-butadine-styrene ("SBS:) block copolymer. Mixtures of two different grades of styrenic thermoplastic elastomer are preferred.

According to a broad aspect of the invention, there is provided an asphalt shingle comprising: a) a base member having a face, the base member comprising a reinforcing web, a bituminous coating applied over the reinforcing web, and mineral granules embedded in the bituminous coating; and b) a bead of sealant composition applied to the face of the base member, the sealant composition comprising a mixture of at least two thermoplastic elastomers and a blown asphalt, the thermoplastic elastomers together comprising from about 5 to 15 percent by weight of the sealant composition, the blown asphalt having a softening temperature of from about 180°F to 230°F, each of the thermoplastic elastomers having a Brookfield viscosity of from 100 to 3000 centipoise at 300°F.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic illustration showing apparatus for application of the improved sealant composition of the present invention to a membrane of roofing material.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The improved shingle of the present invention can include as a base element a glass fiber-reinforcing web saturated with a bituminous material or other material to bind the glass fibers of the web, the web being coated with a layer of a bituminous binder or coating in which an adherent surfacing material comprising mineral granules is embedded. Other types of construction can be employed for the base element. For example, the base element can include multiple layers of bituminous material, in which are adhered different shades, colors, types or sizes of surfacing materials to provide decorative effects or to provide a three-dimensional appearance. Similarly, the base element can be built up of two or more laminated layers, each including a reinforcing web and coated with a bituminous material and having embedded mineral granules. For example, the base element can be built up of a continuous lower layer to which is laminated a discontinuous upper layer, the upper and lower layers each having embedded mineral granules of a size and shade different from the other, the shape of the upper layer being selected to provide a decorative effect. Many different types of construction for the base element will be apparent to those skilled in the art. For example, the base element can include both a laminated second layer having a reinforcing web, as well as an additional layer of bituminous coating material having embedded mineral granules but lacking a reinforcing web.

The base element can include a reinforcing web of a conventional type, such as a woven fabric such as burlap or a nonwoven web of fibrous materials, for example, a nonwoven web or felt of glass fibers, rag fibers, mineral fibers, or the like. The nonwoven web can optionally include a synthetic resin binder or surfacing agent. The web or fabric can be saturated with a bituminous material to bind and weatherproof the fibrous material. Examples of bituminous saturants include asphaltic products such as soft native asphalts, residual oils, soft residual asphalts, soft blown asphalts, petroleum asphalts, soft sludge asphalts, fatty-acid pitches, wool greases, mixtures of one or more of these to obtain a desired consistency, and mixtures of one or more with hardening amounts of harder native asphalts, residual asphalts, or blown petroleum asphalts, and mixtures with softening amounts of vegetable drying or nondrying oils or mineral oils, modified oils such as oxizided linseed oil, synthetic resins, and the like. Further examples of bituminous saturants include tar products including coal tar, water-gas tar, and oil-gas tar, mixtures thereof, and mixtures with corresponding pitches; and mixtures of asphaltic and tar products. Bituminous saturants for roofing webs typically have a low viscosity at the saturating temperature and saturants for webs used in producing shingles typically have fusing points between about 140 °F and 160 °F. The hardness of these saturant materials as measured by penetration at 77 °F is typically greater than about 40 - they are soft materials.

Synthetic resin-type binders for the reinforcing web can also be used, such as synthetic aqueous emulsion-type binders, which include an aqueous dispersion of polymerized ethylenically unsaturated monomers, such as polyvinyl acetate and polyacrylate-type acqueous dispersions produced by emulsion polymerization. Other types of binders which can be employed include water-soluble phenol-formaldehyde resins such as those water soluble resins disclosed in U.S. Patents 4,904,516 and 4,757,108.

The base element can also include an asphaltic coating or binder on at least one surface of the reinforcing web. The asphaltic coating composition can be prepared from the same types of materials employed in preparing the saturant; however, the asphaltic coating composition typically has a harder consistency and a higher fusing point. Examples of bituminous materials from which the asphaltic coating composition can be formed include native asphalts, sludge asphalts, residual asphalts, fatty acid pitches, blown petroleum asphalts, mixtures thereof, and mixtures of the foregoing with oils such as vegetable and mineral oils, modified oils, and the like. Blown petroleum asphalts are preferred. The asphaltic coating composition can include a particulate or fibrous material for filling or stabilizing the composition. Examples of particulate and fibrous fillers include fine grades of silica, calcium carbonate, mica, fly ash, bituminous coal, inorganic fibers such as mineral wool fibers and silica fibers, organic fibers such as cotton, wool, and synthetic fibers, unexpanded vermiculite, and the like.

The first element also includes an adherent surfacing material. The adherent surfacing material is preferably comprised of moderately coarse mineral particles, free from fines, and uniformly sized, and angular in habit. Examples include uncolored granules such as coarsely ground talc, sands, marble, quartz, gravel, feldspar, granite, shale, shell fish shells, and the like; naturally colored slates, greenstone, serpentine, colored sands, basalt, greystone, olivine, and the like; crushed vitrified materials formed from bricks, tiles, glass, slag, and the like; glazed mineral particles; silicated mineral particles such as slate particles treated with sodium silicate solution and insolubilized by heating; mineral granules coated with a hydraulic cement such as a pigmented Portland cement; mineral granules on which inorganic pigments are precipitated; painted mineral granules; chemically treated mineral granules such as slate granules treated with a dichromate solution and subsequently heated; and dyed mineral granules such as clay dyed with an organic dye. A single type of mineral granule can be used, or one or more types of mineral granules can be employed, the types differing in color and/or particle size to achieve desired decorative effects. If more than a single particle type is used, the geometry and distribution of the the different particle types in the asphaltic coating composition can be similarly adjusted to provide desired decorative and aesthetic effects.

The first element can have the shape of an individual shingle or a strip shingle. The manufacture of shingles of a variety of shapes is surveyed in H. Abraham, Asphalts and Allied Substances, Vol. 3, Manufactured Products (D. Van Nostrand Co. Inc. New York, Sixth Ed. 1960), pp. 271-279.

The improved shingle of the present invention can be made by application of the improved sealant composition to the base element directly, or by application of the sealant composition to a continuous web of roofing membrane from which the finished individual shingles are subsequently die cut. An example of this latter process is shown schematically in Figure 1. A continuous web 50 of roofing membrane or "base element" is formed by conventional means (not shown) and passes through an apparatus 10 for application of beads (not shown) of sealant composition 60 to a surface of the web 50, from which individual shingles are subsequently cut (not shown) by conventional means. The sealant composition is provided in drains (not shown) to a drain unloader 24 and fed through a line 26 to a return tank 28 in the direction shown by the arrow 27. The return tank 28 is also fed by another line 40 from a sealant application pan 20 in the direction shown by the arrow 41. Sealant composition is withdrawn from the return tank 28 through a line 30 by a pump 32. The sealant composition flows from the pump 32 through another line 34 in the direction shown by the arrow 35 to a heater 36 and subsequently through yet another line 38 in the direction shown by the arrow 37 to the sealant application pan 20. Sealant composition 60 in the sealant application pan 20 is taken up by a rotating applicator wheel 22, which has a patterned surface, and applied to the surface of the moving membrane 50.

The improved sealant composition includes a bituminous material. This bituminous material can be, for example, selected from those bituminous materials given above as suitable for the asphaltic binder or coating for the base element, or mixture thereof. However, a blown asphalt is preferred. Preferably, the bituminous material of the sealant composition has a softening point or temperature of from about 180°F to 220°F, more preferably from about 195°F to 205°F, with a softening point of about 194° being especially preferred. For example, the bituminous material of the sealant composition can be a standard, steep-grade asphalt (softening point 180°F - 190°F), or a coating-grade asphalt (softening point 190°F - 220°F).

The improved sealant composition also includes a rubbery material, such as an elastomeric, polymeric material. Examples of polymeric materials which can be used include those which are known to improve the physical, low temperature, and durability performance characteristics of asphalt, such as atactic polypropylene (APP), isotactic polypropylene (IPP), styrene-butadiene rubber (SBS), chloroprene rubber (CR), natural and reclaimed rubbers, butadiene rubber (BR), acrylonitrile-butadiene (NBR), isoprene rubber (IR), styrene-polyisoprene (SI), butyl rubber, ethylene propylene rubber (EPR), ethylene propylene diene monomer rubber (EPDM), polyisobutylene (PIB), chlorinated polyethylene (CPE), styrene-ethylene-butylene-styrene (SEBS), and vinylacetate/polyethylene (EVA). Preferably, a thermoplastic elastomer, such as a block copolymer of polystyrene, polybutadiene, and polystyrene blocks is employed.

It is especially preferred that a mixture of two or more grades of thermoplastic elastomer be used. For example, a mixture of two different grades of styrenic thermoplastic elastomer, such as a mixture of two grades having different average particle sizes as reflected by different dilute solution viscosities, can be used. Alternatively, mixtures of different types of styrenic thermoplastic elastomers can be used, such as mixtures of diblock and triblock copolymers.

Examples of styrenic thermoplastic elastomers which can be used in preparing the improved sealant composition of the present invention include styrene-butadiene-styrene block copolymers such as those sold under the Kraton® trademark by Shell Chemical Co., such as Kraton 4460 and Kraton 0-1101, thermoplastic elastomers such as those sold by Phillips Petroleum Co. under the Solprene® trademark, such as Solprene 4755, hydrogenated styrene-butadiene-styrene block copolymers, such as Kraton G-1650, and the like. The styrene thermoplastic elastomers can be block copolymers, such as diblock (A-B) or triblock (A-B-A) copolymers. The block copolymer molecules can be linear, radial, or star-shaped having multiple arms. Individual blocks can by homopolymeric, or copolymeric being polymerized from two or more types of copolymerizible monomers. Suitable styrenic thermoplastic elastomers include styrene-butadiene-styrene, styrene-isoprene-styrene, and styrene-ethylene-butylene-styrene block copolymers.

Preferably, a mixture of two or more styrenic thermoplastic elasticizers is employed, such as a mixture of two or more grades of styrene-butadiene-styrene block copolymers. The grades of styrenic block copolymer can differ in average particle size, average molecular weight, styrene content, molecular geometry (such as in the average number and length of arms for radial block copolymers), or the like. For example, the styrene block copolymers can differ in average molecular weight, as reflected by differing dilute solution viscosities, or like physical properties, and/or in average particles sizes.

Preferably, the rubbery material is predispersed in a blend with one or more additional components to provide the dispersability of the rubbery material in the bituminous material of the improved sealant composition and to promote the compatibility of the rubbery material in the bituminous material. For example, this additive blend can also contain one or more resins such as rosin, rosin derivatives, hydrocarbon resins, cumaron indene resins, polyterpene resins, phenolic resins, hydrogenated rosin esters of polyols, such as pentaerithritol, and the like. Similarly, the additive blend can also include one or more permanent or fugitive plasticizers or oils. Examples of suitable plasticizers include mellitates, phthalate esters such as dioctyl phthalate and di-2-ethyl hexyl phthalate, epoxidized soya bean oils, alkyl epoxy stearates, chlorinated paraffins, petroleum oils, such as high oil cracker bottoms oils, tall oil, and the like.

Preferably, an antioxidant is also included in the additive pre-blend. Examples of suitable antioxidants include dialkyl diphenyl-amine such as dioctyl diphenylamine, aralkyl diphenylamines such as di (alpha,alpha-dimethylbenzyl) diphenylamine, substituted phenols and bisphenols such as polybutylated bisphenol A, substituted aryl phospahtes, substituted mercaptobenzamidoles, and the like.

Preferably, the rubbery material comprises from about 30 to 70 percent by weight of the additive pre-blend composition. It is also preferred that the pre-blend additive composition have a Brookfield viscosity of from about 100 to 3000 centipose at 300°F. If desired, a separate pre-blend composition can be prepared for each thermoplastic elastomer employed in the improved sealant composition. Alternatively, the pre-blend additive composition can comprise a mixture of two or more grades of thermoplastic elastomer. Examples of additive compositions including thermoplastic elastomers suitable for use in preparing the improved sealant compositions of the present invention include those sold by Chemseco Division of Sika Corporation (Kansas City, MO) under the SikaMod™ trademark, such as SikaMod 670, 672, 673, et al. The modifying compositions are preferably blended with the bituminous material at a temperature between about 320°F and 400°F, with agitation sufficient to produce a homogeneous mixture.

Other components which can be added to prepare the sealant composition (either in the additive preblend composition or otherwise) include release agents, microbiocides, colorants, and the like.

After the beads or strips of the improved sealant composition have been applied to the surface of the base element, the beads can be covered with release paper by conventional means.

In the examples which follow, all percentages are by weight and standard ASTM testing procedures were employed where indicated. In addition, the following special test procedures were employed:

TENSILE STRENGTH:

Apparatus:

1. Oven - constant temperature with temperature control between 250°F and 260°F.

2. Paper cutter or die cutter.

3. Testing machine -a) Thwing Albert Model 30LT
b) Instron Tensile Tester

4. Hot plate for wax

Procedure:

A. Thwing-Albert
Jaw distance - 4 inches
Jaw separation speed - 12 inches/minute

B. Instron Tester
Jaw distance - 100mm

Jaw separation speed - 100mm/minute

1. Organic dry felt:

(1) Ten 1" x 6" specimens are cut from each direction of the sample. The 6" direction is to be in the direction to be tested. The specimen should not contain any visible defects such as creases, crush marks, etc.

(2) The ten 1" x 6" specimens are then placed in the oven for at least 15 minutes at a temperature of 250° to 260°F.

(3) Removing one specimen at a time, the specimen is placed loosely in the jaws of the tensile testing machine. It is aligned squarely and then the clamps tightened. (The tensile testing machine and oven should be located as close together as possible so that a minimum amount of time lapses between the time the specimen is removed from the oven and it is tested).

(4) The load of the tensile testing machine is then applied.

(5) The load as recorded on the tensile testing machine at which the specimen breaks is the tensile strength of the specimen. The test result is read to the nearest pound.

(6) The average tensile strength reading from the ten specimens is computed.

(7) Readings obtained when the specimen slips in the jaws or when the break occurs in or near the jaws are to be rejected and an additional specimen is tested.

2. Fiberglass Mat:

(1) Ten 1" x 6" specimens are cut from each direction of the sample. The 6" direction is to be in the direction to be tested. Each machine direction sample should have two reinforcing strands running through the length of the sample. The 1" direction should be cut to an accuracy of ± 1/64 inch. A specimen should be rejected and another cut if the specimen contains any visual defects.

(2) Both ends of the 1" x 6" strips are dipped in liquid paraffin wax to a depth of approximately one inch and allowed to cool. This procedure aids in the prevention of samples slipping out of the jaws of the tensile tester during the time when the load is being applied.

(3) The specimens with the paraffin coated ends are placed loosely in the jaws of the tensile tester. The sample is aligned and the clamps tightened.

(4) The load of the tensile testing machine is then applied.

(5) The load as recorded on the tensile

testing machine at which the specimen breaks is the tensile strength of the specimen. The test result is read to thte nearest pound.

(6) The average tensile strength reading from the ten specimens is computed.

3. Finished product: Same procedure as organic felt except no heating is required.

STIFFNESS-CANTILEVER (Ref. ASTM D747)

Apparatus

1. Tinius-Olsen Stiffness Tester
2. Paper cutter or die cutter

Procedure

1. Place tester on a level surface.
2. Add weights to pendulum.

NOTE: Under normal conditions, shingles are tested with 3 lbs. at room temperature and 6 lbs. at 30°F.

3. Adjust bending span to one inch.
4. Cut 10 specimens 1" x 2½". The 2½" dimension is to be the direction to be tested.
5. Turn tester "on" and leave running throughout the test so as to minimize friction effects.
6. Clamp test specimen in the vise, be sure sample edge is 90° to vise grip.
7. Using the hand crank, apply sufficient load

to show a 1% load reading and then reset the angle pointer to zero.

8. Hold down the motor engaging lever and take subsequent load scale readings at 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90 degree bends. Do not retest a specimen. Do not stop the motor during a test.

9. Plot the data on coordinate paper with the load scale reading as ordinate and the angular deflection as abscissa.

10. If a modulus is to be calculated:

$$E = \frac{4S}{wd^3} \times \left(\frac{ML}{1000}\right)$$

where E = stiffness modulus inlbs. /in.^{2}
S = span length, inch
w = specimen width, inch
d = specimen thickness, inch
M = total load on pendulum
L = scale reading
0 = angular deflection, converted to radians (1 degree = 0.01745 radians)

GRANULE ADHESION

Procedure

A minimum of 3 test specimen shingles are used to calculate scrub loss value.

1. One 2" CD x 9" MD specimen is cut from each of the three sampled shingles.

2. The specimens are dried with a hot air gun. The samples are allowed to cool to room temperature before testing (about 5-10 minutes).

3. Loose granules are removed by dropping the specimen with the long edge horizontal, 4" onto a hard surface.

4. The dry, cool specimen is weighed to the nearest 0.01 g and recorded as "initial weight".

5. The specimen is clamped in the test tray, the brush is gently lowered, and test machine is begun for the 50 cycle test.

6. The sample is removed and dropped with the long edge horizontal, 4" onto a hard surface.

7. The specimen is weighed again to the nearest 0.01 g, and the scrub loss (initial weight - weight after testing) is calculated.

GRANULE ADHESION

a) Dry Rub Test

Ten strips of roofing 2" x 9" are cut lengthwise with the sheet and at equal increment across the sheet. The strips are brushed free of any loose particles and weighed to 0.1 gram. Each strip is in turn clamped in the rubbing machine and given a rub of fifty cycles (fifty forward and fifty backward strokes of the brush). The strips shall then be brushed free of any loose particles and again weighed. The average weight in grams of granules lost per strip is called the "dry loss."

b) Wet Rub Test

Strips are cut out and weighed the same way as in the dry rub test and soaked in tap water at 70°F for 24 hours. At the end of 24 hours one strip at a time is taken from the water and immediately clamped and run on the rub machine and given a fifty cycle rub as in the dry rub test. The strips are then gently immersed in a pan or sink of water to remove loose granules, padded dry and allowed to thoroughly dry at room temperature for 48 hours. The strips are then brushed free of any loose particles and weighed again. The average weight in grams of granules lost per strip is called the "wet loss." This test gives a measure of the embedding as well as the water resistance of the asphalt-to-granule bond.

c) Reseating Test

The strips are cut and soaked as in the "wet rub test." After the 24 hour soaking period the strips are allowed to dry at room temperature for two days. They are then tested for adhesion as in the "dry rub test." The average loss per strip is grams is calculated. The comprision of this figure with the wet loss and dry loss measures the degree of bond between the granule and the asphalt.

BLISTER POTENTIAL

This method imposes below-atmospheric pressure on shingle samples at temperatures well below the

Softening-Point of the coating asphalt for a period of 5 hours. It is designed to produce blistering such as could be expected from normal weather exposure, at an accelerated rate, if the sample has a potential for such blister formation.

Equipment:

vacuum oven - capable of withstanding -30" Hg and maintaining a constant temperature of 60°C. The recommended internal dimensions: 8" height x 8" width x 12" depth. This allows for 6" x 6" samples with 1" clearance from all walls.

vacuum pump - capable of reducing the oven chamber pressure to -27" Hg from atmospheric in less than 5 minutes.

sample pack - capable of carrying 6 samples of shingle/suspended vertically with 1" separating between specimens, and with "guard" specimens intervening between the back wall and the rear specimen, and between the glass observatin door and the most forward specimen.

heating oven - capable of raising the temperature of the samples from ambient to 60°C in from 5 to 7 mins. The operating temperature of this oven should not exceed 70°C during the pre-heating period for the samples.

Procedure:

Samples are 6" x 6" cut from the center portion of a weather tab and include the weather-edge of the tab. If it is felt that there is a problem involving the difference(s) between weather-face and headlap it is recommended that three (3) samples be taken, each 6" x 6"; one from the weather tab; one from the headlap area; and one straddling the line between, i.e. 3" of headlap at the top and 3" of weather-face on the lower half. The samples are punched at the centerline approx ½" down from the top edge of each sample. While in the vacuum oven the sample is suspended from a hook on the rack in such a position that its four edges are approx. one inch from the bottom, sides, and top of the chamber. The temperature of the vacuum overn is stabilized at 60°C under a pressure of -15" Hg. If the test is to be conducted with samples in other than the as-received state such special conditioning shall be noted as the basis for the specific test, and the required pre-conditioning detailed as part of the scope. If samples are to be tested in the as-received state they shall be cut and punched as noted above. Identification should be made on the smooth reverse side, preferably with chalk, but NOT with an oil or wax crayon, nor in such a way as to indent or puncture the back-coating layer. Immediately prior to being placed in the vacuum oven the prepared samples are placed in the pre-conditioning oven and sample temperature raised to 60°C in approx 5 to 7 minutes. With the vacuum oven temperature stabilized at 60°C the vacuum is vented immediately prior to removal of the samples from the pre-conditioning oven. Samples are quickly transferred to the rack, and the rack and samples placed in the vacuum oven with the "guard" samples at back and front. The chamber pressure is reduced to -26" Hg as quickly as possible (preferably in one minute and, in no case more than five minutes) and the pressure and temperature maintained for 5 hours. Occasional observation is made and, if the vacuum is not maintained without adjustment, additional pumping is done to maintain the pressure level. In addition to maintaining the gauge level of pressure, the presence or absence of condensation on the glass door of the vacuum oven should be reported. Note should be made of the initial appearrance (in terms of time elapsed from start of test) and the relative quantity, e.g. light, moderate, or heavy, at the end of the test period. At the end of the 5 hour period the vacuum is vented over a period of approx. 30 secs. and the rack removed from the chamber. The samples are allowed to cool at room temperature. After cooling to room temperature the samples are examined for:

a) Magnitude and frequency of readily visible blisters on both w/face and r/side.

b) Visible back-wetting, "bleeding", or "rain spotting" on r/side.

c) Small blisters faintly discernible and disclosed by penetration with a dental pick.

The blister potential is noted as:

1. Nil, where no blisters are discernible to the eye or with the pick on either w/face or r/side.

2. Light, no large and not more than 6 very small on w/face, and no large nor more than 6 very small on r/side.

3. Moderate, no large and not more than 6 small on w/face, and no large nor more than 12 very small on r/side.

4. Heavy, no more than 6 large nor more than 12 small on w/face, and no large nor more than 36 very small on r/side.

5. Severe, more than 6 large and/or more than 36 small on w/face, or <u>any</u> cratered; any small or more than 36 very small on r/side.

6. Back-wetting is reported as a separate phenomenon.

A major concern relating to modified asphalt compositions is the stability of the final product. Incompatible polymer/asphalt systems tend to separate when stored at high temperatures for long periods of time. Also, depending upon the severity of the incompatibility, phase separation could occur even during short periods of time if no agitation is present. Typically, most of the modified asphalt literature states that asphalts with "low" aromatic content (i.e., oxidized bitumens) tend to be less compatible than their unoxidized counterparts.

A standard compatibility test involves aging a pint-sized sample of the modified bitumen for five days at 320°F. After this aging period, the can is removed and the blend is examined for gross (visible) phase separation. Ultimately, the sample is cut into two equal portions (upper and lower halves) on which softening points and viscosities are determined. The changes in physical properties between the upper and lower halves determine the degree of compatibility between the polymer and asphalt.

After accelerated aging, the upper and lower portions of the blend were examined using fluorescence microscopy, whereby the polymer remained uniformly dispersed. In another compatibility test which utilizes the microscope, thin films of the polymer modified blend are prepared on microscope slides which are subsequently aged at elevated tempertures for four hours. After the aging period, the polymer should remain evenly dispersed with no gross changes in morphology evident.

The following examples will be useful to those skilled in the art in practising the present invention, which is in no way limited thereby.

Example 1

Two additive blend compositions (SikaMod 672 and SikaMod 674) supplied by Chemseco (a division of Sika Corporation, Kansas City MO) were blended into a standard coating grade asphalt (softening point 208°F - 212°F) to yield a sealant composition designed to be more flexible at low temperatures and more squash-out resistant, and to seal at a faster rate than a standard steep sealant. Use of the polymeric additive blend comosition is desirable because unlike neat SBS thermoplastic elastomers, the additive blend compositions are mixed using low shear mixing.

A plant trial was conducted using the improved sealant composition. The improved sealant composition contained five percent by weight SikaMod 672 and five percent by weight SikaMod 674. The physical properties of the improved sealant composition (Example 1) are compared with those of the unmodified asphalt sealant (Comparative Example 1) in Table I below:

Table 1

Example	Comp. 1[1]	1
Softening Point	190°F	208°F
Penetration 32°F	16 dmm.	22 dmm.
Penetration 77°F	28 dmm.	22 dmm.
Penetration 115°F	49 dmm.	49 dmm.
Viscosity 160°C	1540 cps.[2]	5125 cps.
Viscosity 180°C	518 cps.	1390 cps.
Viscosity 190°C	318 cps.	808 cps.
Flash Point, COC	--	505°F
Elongation 20°F	2.5%	12.7%
Modulus 20°F	7310 psi	4120 psi
Ductile - Brittle Temp.	25°F	15°F
Strength 20°F (sealed at 110°F)	7.1 lbs.	15.7 lbs.
Strength 20°F (sealed at 90°F)	2.2 lbs.	4.4 lbs.

---

[1] Comparative Example

[2] Centipoise

The improved sealant composition was prepared by blending as follows:

After taring an empty 55-gallon metal drum, coating grade asphalt was dispensed directly from an asphalt still to the drum. The drum with asphalt was re-weighed and the asphalt and additive weights calculated. Asphalt coming from the still was actually between 490° - 500°F. The longest time constraint was waiting for the asphalt in the drum to cool to 380°F before adding the additive composition. During the cooling period, the asphalt was occasionally agitated by the Greerco high shear mixer (Model 1.5H). Although not necessary to disperse the Chemseco additive compositions, the Greerco mixer was used because of its availability.

When the temperature reached 380°F, the entire additive composition was added to the drum all at once. The temperature decreased to 365°F and remained relatively constant during the half-hour blending period. Samples of the finished sealant composition were removed and tested for consistency (physical properties). The above procedure was repeated until seven 55-gallon drums had been prepared.

Physical properties for each of the seven batches are listed below in Table II.

Table II

Batch No.	1	2	3	4	5	6	7
Softening Pont °F	210	209	208	211	215	211	208
Penetration 32°D dmm.	23	20	21	20	22	23	23
Penetration 77°F dmm.	33	27	36	35	36	35	34
Viscosity 160°C cps.	--	4400	--	--	4938	--	--
Viscosity 180°C cps.	--	1200	--	--	1385	--	--
Viscosity 190°C cps.	--	688	--	--	788	--	--

An entire drum (45 gallons) was pumped through the drum unloader and into the system (as depicted in Figure 1), where the asphalt circulated for 16 hours. Plant personnel had thoroughly cleaned out the sealant pan.

After circulating overnight, a sample of the modified sealant was taken from the return tank and tested, yielding the properties given in Table III below:

Table III

Softening Point = 211°F   Viscosity 160°C = 3800 cps.
Penetration 32°F = 20 dmm.   Viscosity 180°C = 1120 cps.
Penetration 77°F = 30 dmm.   Viscosity 190°C = 625 cps.
Flash Point COC = 515°F

At this time the blend appeared quite smooth without evidence of the air forced into the mixture during high-shear blending. Application of the sealant composition to a web of roofing membrane was then initiated.

The application apparatus shown in Fig. 1 was used. The temperature of the platen of the drum unloader (Nordson) was 375°F. The temperature of the heater (Chromalox) was 355°F. The sealant pan was surrounded with a hot oil jacket maintained at 425°F.

Sealant geometry appeared quite good with well-defined stripes. Although the material is more elastic than the unmodified steep sealant, there was no evidence of "stringing" or "slinging." After two hours into the trial, line speeds were 275 ft./min.

Just prior to the packaging section, an operator constantly scraped sealant build-up on the rolls (from the last shingle in the bundle).

In order to help address this problem, the temperature of the Chromalox heater was lowered from

355°F to 325°F. The lower temperature increased sealant viscosity and improved the sealant application by ensuring a decent caliper on lanes where application was scant.

The trial continued untial seven drums of improved sealant compostion had been applied.

Examples 2-3

A second plant trial was conducted using the improved sealant composition. In this trial, SikaMod 674 and 672 additive compositions were again blended into standard coating asphalt (softening point - 211°F), at a combined level of 15% by weight to give an improved sealant composition (Example 2).

In addition, Imperbel ASD-171 additive composition was blended into a standard sealant asphalt (softening point - 190°F) to give another improved sealant composition (Example 3). All blending was done using a Greeco mixer as above.

The sealant composition of Example 2 included 10 percent by weight SikaMod 674 and 5 percent by weight SikaMod 672. The sealant composition of Example 3 included 15 percent by weight Imperbel ASO-171.

The physical properties of the resulting improved sealant compositions are given in Table IV below and compared with unmodified steep asphalt.

There are significant improvements in low temperature properties (as demonstrated by the modulus, elongation and T-pull data) shown by the sealant composition of Example II.

Table IV

Example	Comp.Ex.2	2	3
Softening Point	190°F	206°F	193°F
Penetration 32°F	16 dmm.	32	24
Penetration 77°F	28 dmm.	45	39
Penetration 115°F	49 dmm.	69	60
Viscosity 160°C	1540 cps.	5963	2250
Viscosity 180°C	518 cps.	1690	875
Viscosity 190°C	318 cps.	1000	588
Flash Point, COC	585°F	480°F	580°F
% Thickness Retained after Squash Out	56	60	57
Tensile Strength 20°F	124psi	72	141
Elongation 20°F	2.5%	10.6%	8.6%
Modulus 20°F	7310 psi	2042	6081
Toughness 20°F	2.0 psi	6.0	11.8
DBTT	25°F	-5°F	10°F
T-Pull 20°F (sealed @ 110°F)	18 lbs. cohesive failure of sealant	42 lbs. shingle delamination	34 lbs. minor shingle delamination
T-Pull 20°F (sealed @ 95°F)	4 lbs.	9 lbs.	19 lbs.
Microscope Slide (after aging)	N.A.	no change	signs of agglomeration evident
Shell Test (compatibility)	N.A.		C.I. = 1.6 S. Pt. = 14°C
Oven-Seal Decks (sealed @ 95°F)	sealed; some sealant transfer	contact seal only	very strong seal; sealant transfer

In accordance with the first sealant trial, the SikaMod additives were added to the asphalt at 380°F and mixed for a half hour, at which time dispersion was complete. Likewise, the Imperbel additive was mixed with asphalt sealant at 380°F, however, complete mixing took 1.5 hours before the materials had been thoroughly blended. Although no mixing problems were encountered in the lab (low shear gaitation), the difficulty in blending the Imperbel additive may, in part, be attributed to its lack of complete compatibility (Table I).

Physical properties for each of the five batches of modified sealant are listed in Table V below:

Table V

Example	2			3	
Batch No.	1	2	3	4	5
Softening Point °F	213	211	211	207	205
Penetration 32°F dmm.	29	30	31	25	24
Penetration 77°F dmm.	42	42	42	38	36
Penetration 115°F dmm.	62	64	63	60	62
Viscosity 160°C cps.	6375	6463	5169	4363	3938
Viscosity 180°C cps.	1615	1625	1458	1343	1275
Viscosity 190°C cps.	920	869	804	821	800

Application of the sealant composition began when the first drum of the sealant of Example 2 was pumped (via Nordson drum unloader; platen temperature = 345°F) through the system as depicted in Figure 1. Unlike the first trial, the Chromalox heater was set for 350°F to accommodate the higher viscosity associated with a 15% polymer blend. Since the sealant pan had not been cleaned out prior to the trial, the first drum was essentially used to purge the system. Collection of shingle samples did not begin until the second Example 2 drum was being pumped. During the trial, line speeds hovered around 280 ft./min., and average sealant calipers taken throughout the day across each lane measured 0.025 inch. The Example 2 trial continued until all material had been applied.

Example 4

In an effort to determine that sealant formulation (optimum polymer level and ideal asphalt softening point) which would yield the optimum performance characteristics -- elongation at low temperatures, strength, ductile-brittle transition temperature, viscosity and squash out, a two level factorial design with full replication and center point was conducted. In this experimental design, polymer levels ranged from 5% to 15%, with the asphalt softening point between 183°F and 201°F. Preliminary work with the Sika additives suggested that the synergistic effect of using both SikaMod 674 and SikaMod 672 actually improved squash-out and enhanced the low temperature properties of the blend more than any single additive. All testing and blend preparation was conducted in a manner which would minimize experimental and bias error. The factorial design indicated that the good sealant characteristics may be obtained by blending 12% of the Sika additives (6% 672 and 6% 674) into an oxidized asphalt having a softening point of 199°F. Similar designed studies conducted with another asphalt source confirm the utility of the Sika additives for use in highly oxidized asphalts to create a modified sealant at polymer loadings between 10%-12%.

Various modifications can be made in the details of the various embodiments of the improved sealant compositions and shingles of the present invention, all within the spirit and scope of the appended claims.

60973-643

CLAIMS:

1. An asphalt shingle comprising:

a) a base member having a face, the base member comprising a reinforcing web, a bituminous coating applied over the reinforcing web, and mineral granules embedded in the bituminous coating; and

b) a bead of sealant composition applied to the face of the base member, the sealant composition comprising a mixture of at least two thermoplastic elastomers and a blown asphalt, the thermoplastic elastomers together comprising from about 5 to 15 percent by weight of the sealant composition, the blown asphalt having a softening temperature of from about 180°F to 230°F, each of the thermoplastic elastomers having a Brookfield viscosity of from 100 to 3000 centipoise at 300°F.

2. A shingle according to claim 1 wherein the blown asphalt has a softening point of from 195°F to 205°F.

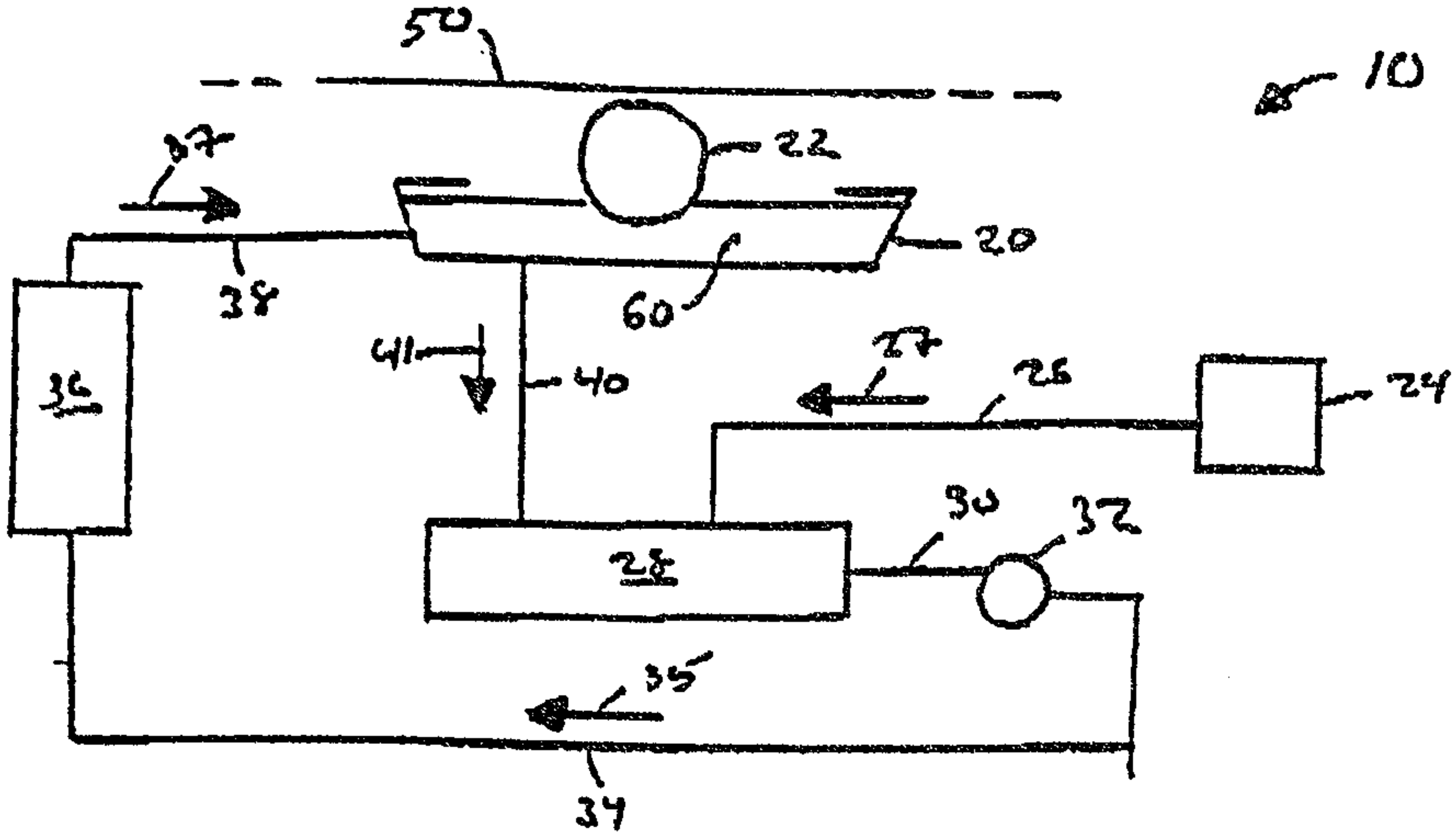
3. A shingle according to claim 1 wherein the mixture of thermoplastic elastomers comprises a mixture of two grades of styrene-butadiene-styrene block copolymers.

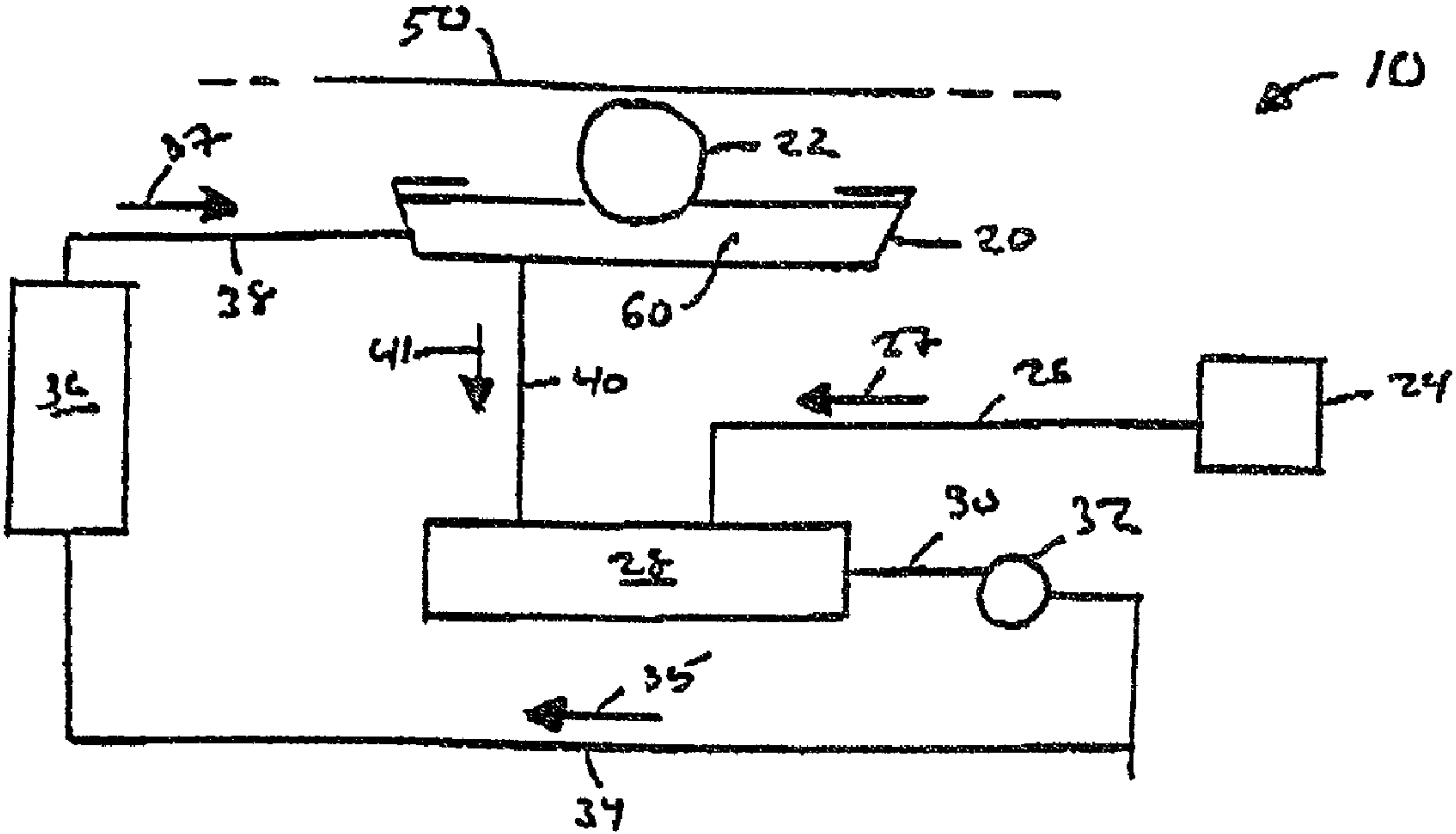
4. A shingle according to claim 1 wherein the sealant composition comprises from 10 to 12 percent by weight of thermoplastic elastomer.

SMART & BIGGAR
OTTAWA, CANADA

PATENT AGENTS

Fig. 1




50
10
22
37
20
38
60
36
41
40
27
26
24
28
30
32
35
34