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# (54) USE OF NANOSIZED PARTICULATES AND FIBERS IN ELASTOMER SEALS FOR IMPROVED PERFORMANCE METRICS FOR ROLLER CONE BITS

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(57) **ABSTRACT**

A bit for drilling subterranean formations that includes a bit body including a bearing surface; a cutting structure mounted on the bit body, and including a bearing surface, and an annular seal for retaining a grease between the bearing surfaces, the annular seal comprising a flexible and resilient seal body formed from an elastomer composition, wherein the elastomer composition comprises an elastomer material, a curing agent, and 10% or less by volume of a nanomaterial additive selected from one of nanotubes and clustered nanodiamonds is disclosed.

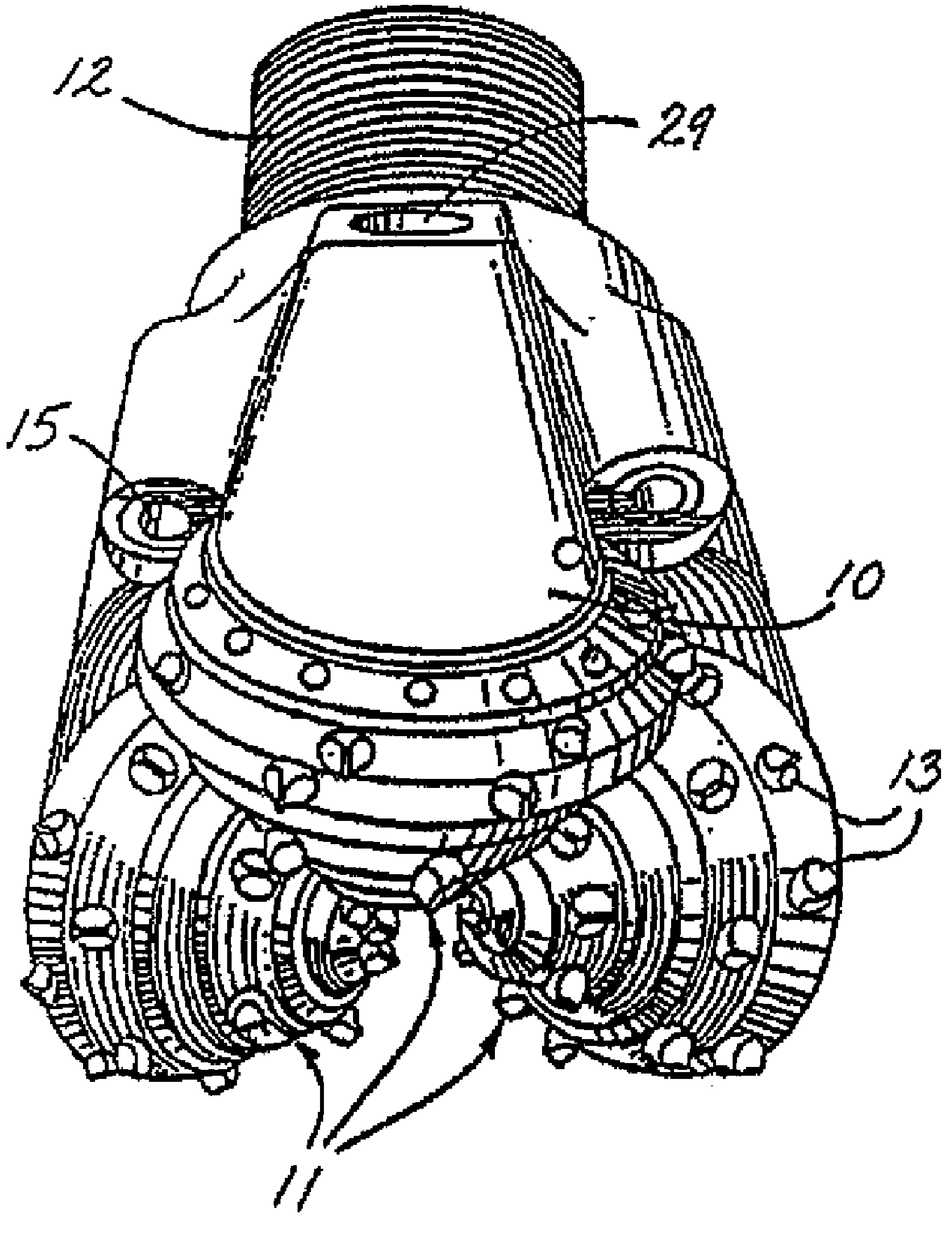

Fig. 1

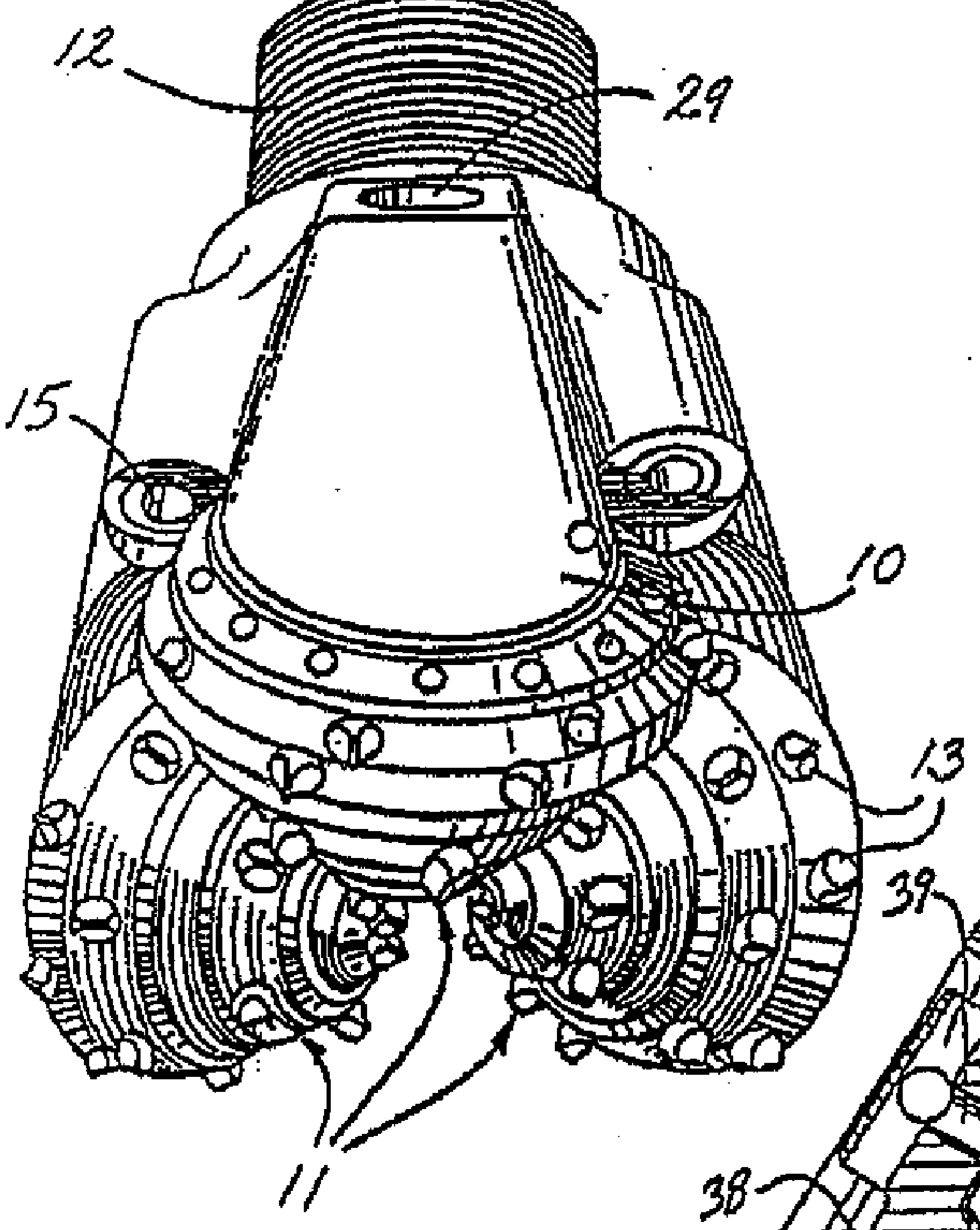
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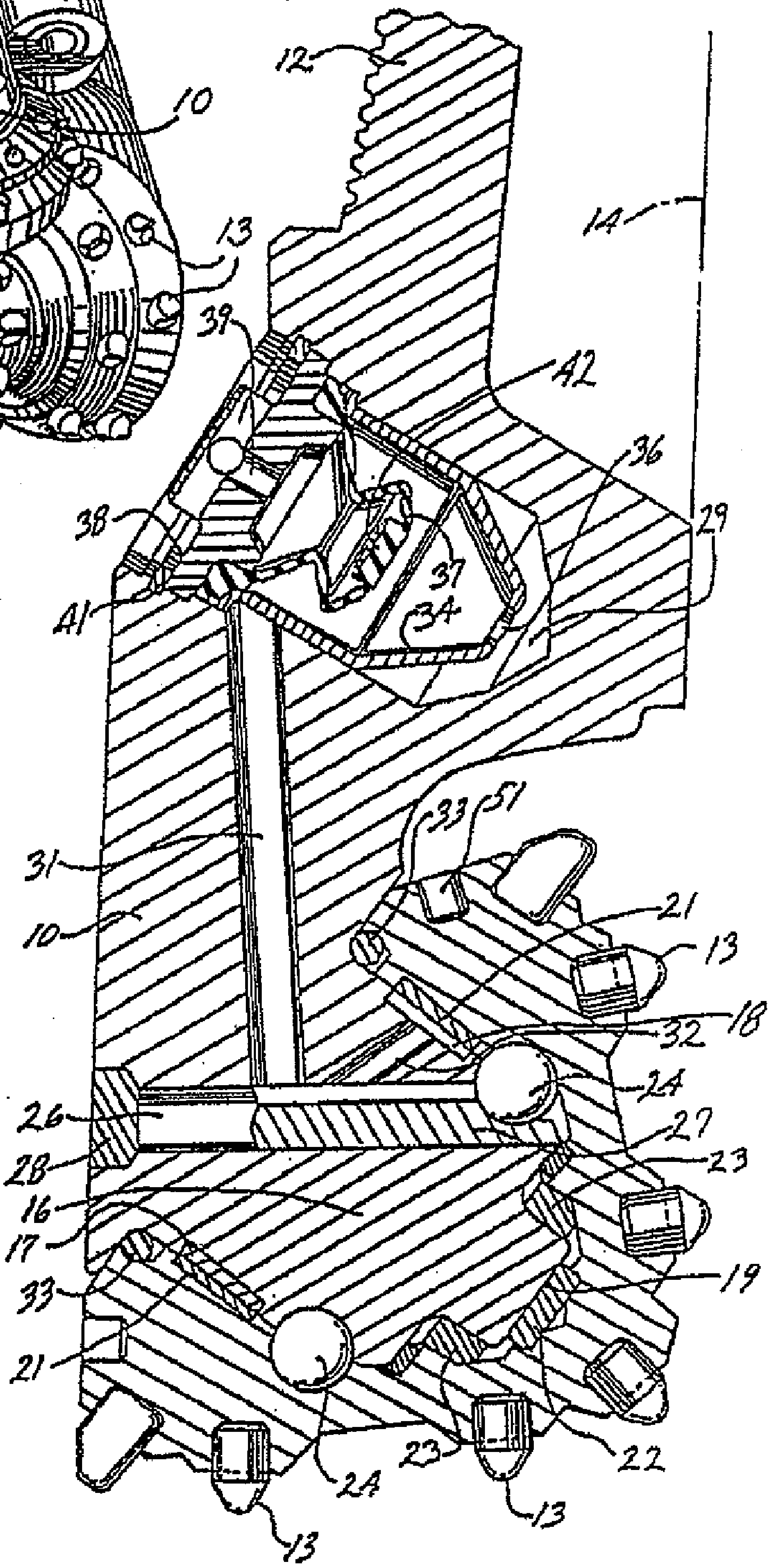
Fig. 2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# USE OF NANOSIZED PARTICULATES AND FIBERS IN ELASTOMER SEALS FOR IMPROVED PERFORMANCE METRICS FOR ROLLER CONE BITS

## CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** This application, pursuant to 35 U.S.C. §119(e), claims priority to U.S. Patent Application No. 60/954,272, filed on Aug. 6, 2007, which is herein incorporated by reference in its entirety.

## BACKGROUND OF INVENTION

**[0002]** 1. Field of the Invention

**[0003]** Embodiments disclosed herein relate generally to the use of composite materials in seals for cutting tools. More particularly, embodiments disclosed herein relate to the incorporation of nanosized particulates and fibers into elastomer seals for improved wear resistance, thereby enhancing the performance and service life of the roller cone bit.

**[0004]** 2. Background Art

**[0005]** Drill bits are commonly used in, for example, the oil and gas exploration industry for drilling wells in earth formations. One type of drill bit commonly used in the industry is the roller cone drill bit. Roller cone drill bits generally comprise a bit body connected to a drill string or bottom hole assembly (BHA). Roller cone drill bits typically include a plurality of roller cones rotatably attached to the bit body. The roller cones are generally mounted on steel journals integral with the bit body at its lower end. The roller cones further comprise a plurality of cutting elements disposed on each of the plurality of roller cones. The cutting elements may comprise, for example, inserts (formed from, for example, polycrystalline diamond, boron nitride, and the like) and/or milled steel teeth that are coated with appropriate hardfacing materials.

**[0006]** When drilling an earth formation, the roller cone drill bit is rotated in a wellbore, and each roller cone contacts the bottom of the wellbore being drilled and subsequently rotates with respect to the drill bit body. Drilling generally continues until, for example, a bit change is required because of a change in formation type is encountered in the wellbore or because the drill bit is worn and/or damaged. High temperatures, high pressures, tough, abrasive formations, and other factors all contribute to drill bit wear and failure.

**[0007]** When a drill bit wears out or fails as the wellbore is being drilled, it is necessary to remove the BHA from the well so that the drill bit may be replaced. The amount of time required to make a bit replacement trip produces downtime in drilling operations. The amount of downtime may be significant, for example, when tripping in and out of relatively deep wells. Downtime may be add to the cost of completing a well and is a particular problem in offshore operations where costs are significantly higher. It is therefore desirable to maximize the service life of a drill bit in order to avoid rig downtime.

**[0008]** One reason for the failure of a roller cone drill bit is the wear that occurs on the journal bearings that support the roller cones. The journal bearings may be friction-type or roller-type bearings, and are subjected to high loads, high pressures, high temperatures, and exposure to abrasive particles originating from the formation being drilled. The journal bearings are typically lubricated with grease adapted to withstand tough drilling environments. Thus, such lubricants are an important element in the life of a drill bit.

**[0009]** Lubricants are retained by a journal bearing seal, which is typically an O-ring type seal, typically located in a seal groove formed on an interior surface of a roller cone. The seal generally includes a static seal surface adapted to form a static seal with the interior surface of the roller cone and a dynamic seal surface adapted to form a dynamic seal with the journal upon which the roller cone is rotatably mounted. The seal must endure a range of temperature and pressure conditions during the operation of the drill bit to prevent lubricants from escaping and/or contaminants from entering the journal bearing. Elastomer seals known in the art are conventionally formed from a single type of rubber or elastomer material, and are generally formed having identically configured dynamic and static seal surfaces with a generally regular cross section.

**[0010]** The rubber or elastomer material selected to form the seal for the journal hearings has particular hardness, modulus of elasticity, wear resistance, temperature stability, and coefficient of friction, among other properties. Additionally, the particular geometric configuration of the seal surfaces produces a selected amount of seal deflection that defines the degree of contact pressure or "squeeze" applied by the dynamic and static seal surfaces against respective Journal bearing and roller cone surfaces.

**[0011]** The wear, temperature, and contact pressures encountered at the dynamic seal surface are different than those encountered at the static seal surface. Therefore, the type of seal material and seal geometry that is ultimately selected to form both seal surfaces represents a compromise between satisfying the operating conditions that occur at the different dynamic and static seal surfaces.

**[0012]** Conventional seals formed from a single-type of material, having symmetric axial cross-sectional geometries, may have reduced wear resistance and temperature stability at the dynamic seal surface where wear and temperature conditions are generally more severe than at the static seal surface. Therefore, the service life of drill bits that contain such seals may be limited by the service life of the journal bearing seal. It is desirable to produce a seal that is capable of withstanding the harsh downhole conditions, such as high pressures and temperatures. Accordingly, there exists a need for a tough, long-lasting seal, and drill bits containing such seals.

## SUMMARY OF INVENTION

**[0013]** In one aspect, embodiments disclosed herein relate to a bit for drilling subterranean formations that includes a bit body including a bearing surface; a cutting structure mounted on the bit body, and including a bearing surface, and an annular seal for retaining a grease between the bearing surfaces, the annular seal comprising a flexible and resilient seal body formed from an elastomer composition, wherein the elastomer composition comprises an elastomer material, a curing agent, and 10% or less by volume of a nanomaterial additive selected from one of nanotubes and clustered nanodiamonds.

**[0014]** In another aspect, embodiments disclosed herein relate to a rock bit for drilling subterranean formations that includes a bit body including at least one journal pin, each having a bearing surface; a roller cone mounted on the at least one journal pin and including a bearing surface; an annular seal for retaining a grease between the bearing surfaces, the annular seal comprising a flexible and resilient seal body formed from an elastomer composition, wherein the elastomer composition comprises: 100 parts by weight of highly saturated nitrile elastomer; furnace black in the range of up to 70 parts by weight; peroxide curing agent in the range of from 7 to 10 parts by weight; zinc oxide in the range of from 4 to 7 parts by weight; stearic acid in the range of from 0.5 to 2 parts by weight; nanomaterial additives selected from one of nanotubes and clustered nanodiamonds in the range of up to 10 percent by volume, and sufficient plasticizer to provide a Shore Hardness of no more than A 80.

**[0015]** Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

## BRIEF DESCRIPTION OF DRAWINGS

**[0016]** FIG. **1** is a semi-schematic perspective of a drill bit according to one embodiment of the present invention.

**[0017]** FIG. **2** is a partial cross-section of the drill bit according FIG. **1**.

## DETAILED DESCRIPTION

**[0018]** In one aspect, embodiments disclosed herein relate to elastomer seals used in components of downhole cutting tools, including drill bits, core bits, etc. In particular, embodiments disclosed herein relate to seals reinforced with nanomaterials.

**[0019]** In addition, embodiments of the present disclosure provide rock bits comprising seals which are reinforced by nanomaterials. Such a reinforced seal may have enhanced bulk properties such as tensile modulus, elastic modulus, hardness, and such like, as compared with the native seal, while maintaining wear and erosion resistance. Embodiments of the present disclosure are based, in part, on the determination that the life of a seal is directly related to the service life of the rock bit.

**[0020]** It is therefore desirable to provide a consistently reliable seal for maintaining the lubricant within a rock bit, where the seal has a long useful life, is resistant to oil well chemical compositions, has high heat resistance, and is highly resistant to abrasion.

**[0021]** Referring to FIG. **1**, a drill bit in accordance with an embodiment of the invention is shown. In this embodiment, as shown in FIG. **1**, a drill bit **5** comprises a body **10** having three roller cones **11** mounted on its lower end. A threaded pin **12** is at the upper end of the body **10** for assembly of the drill bit **5** onto a drill string (not shown separately) for drilling oil wells or the like. A plurality of cutting elements **13** are pressed into holes in the surfaces of the roller cones **11** for bearing on the rock formation being drilled. Nozzles **15** in the bit body **10** introduce drilling mud into the space around the roller cones **11** for cooling and carrying away formation chips drilled by the drill bit **5**. While reference is made to an insert-type bit, the scope of the present invention should not be limited by any particular cutting structure. Embodiments of the present invention generally apply to any rock bit (whether roller cone, disc, etc.) that requires an elastomer seal to retain grease.

**[0022]** FIG. **2** shows a part of a longitudinal cross section of the drill bit **5** of FIG. **1**, extending radially from the rotational axis **14** of the rock bit through one of the three legs on which the roller cones **11** are mounted. Each leg includes a journal **16** extending downwardly and radially inwardly on the rock bit body **10**. The journal **16** includes a cylindrical bearing surface having a hard metal insert **17** on a lower portion of the journal **16**.

**[0023]** Each roller cone **11** is in the form of a hollow, frustoconical steel body having cutting elements **13** pressed into holes on the external surface. For long life, the cutting elements **13** may be tungsten carbide inserts tipped with a polycrystalline diamond layer. Such tungsten carbide inserts provide the drilling action by engaging a subterranean rock formation as the rock bit is rotated. Some types of bits have hard-faced steel teeth milled on the outside of the cone instead of carbide inserts.

**[0024]** The cavity in the cone **11** contains a cylindrical bearing surface including a copper nickel tin insert **21** deposited in a groove in the steel of the cone **11** or as a floating insert in a groove in the cone **11**. The alloy insert **21** in the cone **11** engages the hard metal insert **17** on the leg and provides the main bearing surface for the cone **11** on the bit body **10**. A nose button **22** is between the end of the cavity in the cone **11** and the nose **19** and carries the principal thrust loads of the cone **11** on the journal **16**. A bushing **23** surrounds the nose and provides additional bearing surface between the cone **11** and journal **16**. Other types of bits, particularly for higher rotational speed applications, may have roller bearings instead of the exemplary journal bearings illustrated herein.

**[0025]** A plurality of bearing balls **24** are fitted into complementary ball races in the cone **11** and on the journal **16**. These balls **24** are inserted through a ball passage **26**, which extends through the journal **16** between the bearing races and the exterior of the drill bit **5**. A cone **11** is first fitted on the journal **16**, and then the bearing balls **24** are inserted through the ball passage. The balls **24** carry any thrust loads tending to remove the cone **11** from the journal **16** and thereby retain the cone **11** on the journal **16**. The balls **24** are retained in the races by a ball retainer **27** inserted through the ball passage **26** after the balls are in place. A plug **28** is then welded into the end of the ball passage to keep the ball retainer in place.

**[0026]** The bearing surfaces between the journal **16** and cone **11** are lubricated by a lubricant or grease composition. Preferably, the interior of the drill bit is evacuated and lubricant or grease is introduced through a fill passage (not shown separately). The lubricant or grease thus fills the regions adjacent the bearing surfaces plus various passages and a grease reservoir. The grease reservoir comprises a cavity **29** in the bit body **10**, which is connected to the ball passage **26** by a lubricant passage **31**. Lubricant or grease also fills the portion of the ball passage **26** adjacent the ball retainer, the open groove **18** on the upper side of the journal **16**, and a diagonally extending passage **32** therebetween. Lubricant or grease is retained in the bearing structure by a resilient and flexible seal **33** between the cone **11** and journal **16**.

**[0027]** A pressure compensation subassembly is included in the grease reservoir **29**. This subassembly comprises a metal cup **34** with an opening **36** at its inner end. A flexible rubber bellows **37** extends into the cup **34** from its outer end. The bellows **37** is held in place by a cap **38** with a vent passage **39**. The pressure compensation subassembly is held in the grease reservoir by a snap ring **41**.

**[0028]** When the drill bit is filled with lubricant or grease, the bearings, the groove **18** on the journal **16**, passages in the journal **16**, the lubrication passage **31**, and the grease reservoir on the outside of the bellows **37** are filled with lubricant or grease. If the volume of lubricant or grease expands due to heating, for example, the bellows **37** is compressed to provide additional volume in the sealed grease system, thereby preventing accumulation of excessive pressures. High pressure in the grease system may be damage the seal **33** and permit abrasive drilling mud or the like to enter the bearings. Conversely, if the grease volume should contract, the bellows **37** may be expand to prevent low pressures in the sealed grease systems, which could cause flow of abrasive and/or corrosive substances past the seal **33**.

**[0029]** To maintain the desired properties of the seal at the harsh pressure and temperature conditions prevalent in a rock bit, to inhibit undesired pumping of lubricant through the seal, and to promote a long and useful life, it is desirable that the seal be chemically and physically resistant to chemical compositions found downhole, have a high heat and abrasion resistance, have a low rubbing friction, and not be readily deformed under the pressure and temperature conditions found in a well. Therefore, for certain applications it is desirable that the seal have a modulus of elasticity at 100% elongation from 800 to 1275 psi, a minimum tensile strength of 2300 psi, elongation from 200 to 300 percent, die C tear strength of at least 250 lbs/inch, durometer hardness Shore A in the range from 75 to 85, and a compression set after 70 hours at 100° C. of less than about 18% and preferably about 16%.

**[0030]** A variety of seals have been employed in such rock bits. These seals usually are made of synthetic rubbers. Other components in the seal are usually curing agents, other additives such as plasticizers, fillers, coagents, accelerators, retardants, antioxidants and lubricants. Seals of the type found in embodiments of the present disclosure further comprise nanomaterial additives.

**[0031]** Polymers and Elastomer Materials

**[0032]** Seals typically used in rock bits are usually made of acrylontrile polymers or acrylonitrile/butadiene copolymers. However, these synthetic rubbers typically exhibit poor heat resistance and become brittle at elevated temperatures after extended periods of time. Additionally, these rubbers often exhibit undesirably low tensile strength and high coefficients of friction. Such properties are undesirable in a seal to be used in a rock bit, because the high operating temperatures of the bit may be result in failure of the seal.

**[0033]** Preferred seals may be formed from elastomer compositions such as fluoroelastomers, carboxylated nitriles, highly saturated nitrite (HSN) elastomers, nitrile-butadiene rubbers, highly saturated nitrile-butadiene rubbers (HNBR), fluorocarbons, ethylene-propylenes, silicones, chloroprenes, neoprenes, fluorosilicones, polyurethanes, perfluoroelastomers, polyacrylates, copolymers of tetrafluoroethylene and propylene, ethylene-acrylic rubbers, chlorosulfonyl polyethylene rubbers, epichlorohydrin polymers, styrene butadiene polymers, and mixtures or copolymers thereof.

**[0034]** HSM elastomer seals are disclosed in U.S. Pat. No. 5,323,863, which is assigned to the same assignee as the present disclosure and is hereby incorporated by reference. An exemplary elastomer composition may comprise per 100 parts by weight of elastomer (e.g. HSN, HNBR, etc.), furnace black in the range of from 40 to 70 parts by weight, peroxide curing agent in the range of from 7 to 10 parts by weight, graphite in the range from 10 to 20 parts by weight, zinc oxide or magnesium oxide in the range of from 4 to 7 parts by weight, stearic acid in the range from 0.5 to 2 parts by weight, and plasticizer up to about 10 parts by weight.

**[0035]** In elastomer materials, the tensile modulus of the elastomer, its tear strength, and its hardness are positively correlated. As such, when the hardness of the elastomer is increased, one normally finds that the tear strength and tensile modulus similarly increase. Hardness is therefore a convenient method to compare elastomer compositions.

**[0036]** The hardness of an elastomer material is defined as the material's ability to withstand indentation. Durometer is typically used as a measure of hardness for polymers, elastomers, and rubbers, and is described in U.S. Pat. No. 1,770, 045 issued to A. F. Shore. Commonly called the Shore hardness, durometer is measured using the ASTM D2240-00 testing standard. There are a total of 12 scales, depending on the intended use: types A, B, C, D, DO, E, M, O, OO, OOO, OOO—S, and R. The A scale is usually reserved for softer plastics, while the D scale is for harder ones. Each scale results in a value between 0 and 100, with higher values indicating a harder material. For a rock bit seal, it is desirable that the durometer hardness is in the range of from about 75 to 85 on the Shore A scale. A hardness of 85 or higher may result in premature failure of the seal.

**[0037]** Curing Agents

**[0038]** Curing refers the thickening or hardening of a polymer material, which is also called vulcanization when the polymer is rubber. Curing agents are agents or substances added to a polymer composition to promote or control the curing reaction, either catalytically or as a reactant, such as cross-linkers, heat, electron beam, UV radiation, or chemical catalysts.

**[0039]** In some embodiments, the catalyst may include organometallic catalysts such as organic complexes of Sn, Ti, Pt, Pb, Sb, Zn, or Rh, inorganic oxides such as manganese (IV) oxide, calcium peroxide, or lead dioxide, and combinations thereof, metal oxide salts such as sodium perborates and other borate compounds, or organic peroxides such as cumene hydroperoxide. In a particular embodiment, the organometallic catalyst may be dibutyltin dilaurate, a titanate/zinc acetate material, tin octoate, a carboxylic salt of Pb, Zn, Zr, or Sb, and combinations thereof.

**[0040]** The catalyst may be present in an amount effective to catalyze the curing of the liquid elastomer composition. In various embodiments, the catalyst may be used in an amount ranging from about 0.01 to about 10 weight percent, based on the total weight of the elastomer(s), from about 0.05 to about 5 weight percent in other embodiments, and from about 0.10 to about 2 weight percent in yet other embodiments.

**[0041]** In general, the crosslinker may be any nucleophilic or electrophilic group that may react with the reactive groups available in the elastomer composition. In a further embodiment, the crosslinking agent may comprise a polyfunctional molecule with more than one reactive group. Such reactive groups may include for example, amines, alcohols, phenols, thiols, carbanions, organofunctional silanes, and carboxylates.

**[0042]** Other Additives

**[0043]** Additives are widely used in elastomer compositions to tailor the physical properties of the resultant elastomer composition. In some embodiments, additives may include accelerators and retardants, plasticizers, thermal and light stabilizers, flame-retardants, fillers, adhesion promoters, or Theological additives.

**[0044]** Accelerators and retardants may optionally be used to control the cure time of the liquid elastomer. For example, an accelerator may be used to shorten the cure time while a retardant may be used to prolong the cure time. In some embodiments, the accelerator may include an amine, a sulfonamide, or a disulfide, and the retardant may include a stearate, an organic carbamate and salts thereof, a lactone, or a stearic acid.

**[0045]** Addition of plasticizers may reduce the modulus of the polymer at the use temperature by lowering its Tg. This may allow control of the viscosity and mechanical properties of the elastomer seal. In some embodiments, the plasticizer may include phthalates, epoxides, aliphatic diesters, phosphates, sulfonamides, glycols, polyethers, trimellitates or chlorinated paraffin. In some embodiments, the plasticizer may be a diisooctyl phthalate, epoxidized soybean oil, di-2-ethylhexyl adipate, tricresyl phosphate, or trioctyl trimellitate.

**[0046]** Fillers are usually inert materials which may reinforce the elastomer seal or serve as an extender. Fillers therefore affect elastomer processing, storage, and curing. Fillers may also affect the properties of the elastomer such as electrical and heat insulting properties, modulus, tensile or tear strength, abrasion resistance and fatigue strength. In some embodiments, the fillers may include carbonates, metal oxides, clays, silicas, mica, metal sulfates, metal chromates, or carbon black. In some embodiments, the filler may include titanium dioxide, calcium carbonate, non-acidic clays, or fumed silica.

**[0047]** Addition of adhesion promoters may improve adhesion to various substrates. In some embodiments, adhesion promoters may include epoxy resins, modified phenolic resins, modified hydrocarbon resins, polysiloxanes, silanes, or primers.

**[0048]** Addition of rheological additives may control the flow behavior of the compound. In some embodiments, Theological additives may include fine particle size fillers, organic agents, or combinations of both. In some embodiments, Theological additives may include precipitated calcium carbonates, non-acidic clays, famed silicas, or modified castor oils.

**[0049]** Nanomaterial Additives

**[0050]** Nanomaterials possess dimensions on the order of a billionth of a meter. In a particular embodiment, the nanomaterial additive may have dimensions ranging from about 0.1 to 100 nanometers. In another embodiment, the nanomaterial may have dimensions ranging from 0.5 to 50 nanometers. In yet another embodiment, the nanomaterial may have dimensions ranging from about 1.0 to 10 nanometers.

**[0051]** Nanomaterials typically have a very high aspect ratio, that is, the ratio of length to diameter. In a particular embodiment, the nanomaterials used in the present disclosure may have an aspect ratio ranging from about 1.0 to 1,000,000. In one embodiment, the nanomaterial may have an aspect ratio ranging from 1.0 to 300. In yet another embodiment, the nanomaterial may have an aspect ratio ranging from 3.0 to 100.

**[0052]** In particular embodiments, the at least one nanomaterial additive may be selected from at least one of nanoclays, carbon nanotubes, functionalized nanotubes, inorganic nanotubes, clustered nanodiamonds, fullerenes, other inorganic nanomaterial additives, and mixtures thereof. Nanomaterial additives may be added to elastomer composition disclosed herein in an amount greater than about 0.1, 0.2, 0.3, 0.5, 1, and 2 volume percent in some embodiments, and less than 10, 5, 4, 2, and 1 volume percent in other embodiments.

**[0053]** Nanoclays

**[0054]** The nanoclay raw material may be montmorillonite (magnesium aluminum silicate) or bentonite (aluminum phyllosilicate), a 2-to-1 layered smectite clay mineral with a platy or tubular structure. Individual plate thickness of nanoclays may be just one nanometer, but the surface dimensions may generally range from about 300 to more than 600 nanometers, resulting in an unusually high aspect ratio. Naturally occurring montmonrllonite is hydrophilic. Since polymers are generally organophilic, unmodified nanoclays disperse in polymers with great difficulty. Through clay surface modification, montmorillonite may be made organophilic and, therefore, compatible with conventional organic polymers.

**[0055]** A number of chemistries may be conventionally applied to modify the surfaces of nanoclays. For example, in the traditional "onuim ion" modification, a clay-chemical complex is formed using an intercalant (surface treatment) containing an ammonium or phosphonium functional group. These groups modify the nanoclay surface by ionically bonding to it, thereby converting the surface from a hydrophilic to an organophilic species.

**[0056]** Other means for modification involve leaving the sodium ion on the surface and coordinating it via ion-dipole interaction. Regardless of the modification technology used, the resulting clay-chemical complex, which exhibits a definite gallery spacing between the plates, may be easily dispersed in a polymer matrix to form a nanocomposite material.

**[0057]** In some embodiments, nanoclays are dispersed into the elastomer composition of the seal body, generally at less than 5 wt % levels. When a nanoclay is substantially dispersed within the polymer it is said to be exfoliated. Exfoliation is facilitated by surface modification chemistries described above, which through ionic interactions, separate the nanoclay plates to the point where individual plates may be further separated from another by mechanical shear or heat of polymerization. Nanocomposites may be created using both thermoplastic and thermoset polymers, and the specific surface modification chemistries designed and employed are necessarily a function of the host polymer's unique chemical and physical characteristics. In some cases, the final nanocomposite will be prepared in the reactor during the polymerization stage. For other polymer systems, processes may be used to incorporate nanoclays into a hot-melt compounding operation.

**[0058]** In general, nanocomposites exhibit gains in barrier, flame resistance, structural, and thermal properties yet without significant loss in hardness or clarity. Because of the nanometer-sized dimensions of the individual plates in one direction, exfoliated nanoclays are transparent in most polymer systems. However, with surface dimensions extending to 1 micron, the tightly bound structure in a polymer matrix is impermeable to gases and liquids, and offers superior barrier properties over the native polymer. Such nanocomposites may also exhibit enhanced heat resistive properties.

**[0059]** Nanoclays are commercially available as Nanomer® nanoclays from Nanocor®, Cloisite® additives from Southern Clay Products, Nanolin from FCC Inc., Halloysite from Nanoclay Technologies.

**[0060]** Fullerenes and Nanotubes

**[0061]** Fullerenes are a family of carbon allotropes named after Richard Buckminster Fuller and are sometimes called buckyballs. They are closed cages molecules composed entirely of $sp^2$-hybridized carbons and may be in the form of a hollow sphere, ellipsoid, or tube. Cylindrical fullerenes are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of a sheet of linked hexagonal rings, but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. Fullerenes may be produced by carbon arc methods of condensation of vaporized carbon.

**[0062]** As used herein, the term "nanotube" refers to various materials having having a cylindrical or tubular configuration with at least one dimension, such as length or diameter, between 1 and 100 nanometers. Types of nanotubes that may find use as a reinforcing nanotubes material in the present disclosure may include carbon nanotubes (CNTs), including single-walled (SWNT), double-walled (DWNT), multi-walled (MWNT), inorganic nanotubes, multibranched nanotubes, functionalized nanotubes, and CNT-$C_{60}$ hybrids. Additionally, in some embodiments, at least a portion of the surface of the reinforcing nanotubes may be modified.

**[0063]** Carbon nanotubes are polymers of pure carbon, which may be functionalized or otherwise modified. Both SWNTs and MVVNTs are known in the art and the subject of a considerable body of published literature. Examples of literature on the subject are Dresselhaus, M. S., et al., Science of Fullerenes and Carbon Nanotubes, Academic Press, San Diego (1996), and Ajayan, P- M., et al., "Nanometre-Size Tubes of Carbon," Rep. Prog. Phys. 60 (1997); 1025-1062. The structure of a single-wall carbon nanotube may be described as a single graphene sheet rolled into a seamless cylinder whose ends are either open or closed. When closed, the ends are capped by either half fullerenes or more complex structures including pentagons.

**[0064]** Nanotubes frequently exist as "ropes," or bundles of 10 to 100 nanotubes held together along their length by van der Waals forces, with individual nanotubes branching off and joining nanotubes of other "ropes." Multi-walled carbon nanotubes are multiple concentric cylinders of graphene sheets. The cylinders are of successively larger diameter to fit one inside another, forming a layered composite tube bonded together by van der Waals forces, with a typical distance of approximately 0.34 nm between layers, as reported by Peigney, A., et al., "Carbon nanotubes in novel ceramic matrix nanocomposites," Ceram. Inter. 26 (2000) 677-683.

**[0065]** Carbon nanotubes are commonly prepared by arc discharge between carbon electrodes in an inert gas atmosphere. The product is generally a mixture of single-wall and multi-wall nanotubes, although the formation of single-wall nanotubes can be favored by the use of transition metal catalysts such as iron or cobalt. The electric arc method, as well as other methods for the synthesis of carbon nanotubes is described in, for example, "Nanometre-Size Tubes of Carbon," P. M. Ajayan and T. W. Ebbesen, Rep. Prog. Phys., 60, 1025-1062 (1997). Inorganic nanotubes may include those prepared from a range of materials including boron nitride, silicon nitride, silicon carbide, dichalcogenides, for example, $WS_2$, oxides such as $HfO_2$ and $MoO_3$, metallic nanotubes, such as Co and Au, and materials having a composition $B_xC_yN_z$, where x, y, and z may be independently selected from 0 to 4, including for example, $BC_2N_2$ and $BC_4N$, and combinations thereof.

**[0066]** In a particular embodiment, the average diameter of the nanotube materials may range from about 1 to 100 nanometers. In various other embodiments, the reinforcing phase may include SWNTs having an average diameter of about 1 to 2 nanometers and/or MWNTs having an average diameter of about 2 to 30 nanometers. Nanotube materials typically have a very high aspect ratio. In a particular embodiment, the nanotubes used in the present disclosure may have an aspect ratio ranging from about 25 to 1,000,000, and preferably from about 100 to about 1,000.

**[0067]** The surface of the carbon nanotubes of fullerene may, in one embodiment, be modified prior to incorporation into the composites of the present disclosure. In some embodiments, the nanostructured carbon material is modified by a chemical means to yield derivatized nanostructured carbon material. As used herein, "derivatization" refers to the attachment of other chemical entities to the nanostructured carbon material, which may be by chemical or physical means including, but not limited to, covalent bonding, van der Waals forces, electrostatic forces, physical entanglement, and combinations thereof. In other embodiments, the nanostructured carbon material is modified by a physical means selected from the group consisting of plasma treatment, heat treatment, ion bombardment, attrition by impact, milling and combinations thereof In yet other embodiments, the nanostructured carbon material is modified by a chemical means selected from the group consisting of chemical etching by acids either in liquid or gaseous form, chemical etching by bases either in liquid or gaseous form, electrochemical treatments, and combinations thereof.

**[0068]** One of ordinary skill in the art would appreciate that derivatization or functionalization may be desired so as to increase ease in solubilization and/or disperson of the nanotubes into at least one of the component phases prior to formation of a composite material. Functionalization or derivatization may occur by the incorporation of various chemical moieties on either end caps and/or sidewalls (either exterior or interior) of the nanostructured carbon material, or with a coating placed thereon.

**[0069]** For example, functionalization may occur through covalent and/or non-covalent functionalization, endcap and/or sidewall functionalization, exohedral and/or endohedral functionalization and supramolecular complexation. A variety of functionalized nanostructured carbon materials have been developed so as to enable dispersion of the nanostructures into composite materials, including fluoronanotubes, carboxy-nanotubes, and various covalently bonded nanotubes, including amino-CNTs, vinyl-CNTs, epoxy-CNTs. Oxidation of nanostructured carbon materials may result in carboxyl, hydroxyl, or carbonyl groups, which may be further modified via amidation or etherification, for example. Additionally, functionalization frequently occurs through an initial fluorination, and then subsequent nucleophilic attack, or via a free radical reaction to form a covalent carbon-carbon bond. Further, U.S. Pat. Nos. 7,122,165, 7,105,596, 7,048,999, 6,875,412, 6,835,366, 6,790,425, 2005/0255030, which are all herein incorporated by reference in their entirety, disclose various sidewall and endcap functionalization that may, for example, be used to assist in integration of nanostructured carbon materials in an elastomer seal of the present disclosure. Nanostructured carbon materials may be added to elastomer seals disclosed herein in an amount greater than about 0.1, 0.2, 0.5, 1, and 2 volume percent in some embodiments, and less than 10, 5, 4, 2, and 1 volume percent in other embodiments.

**[0070]** Other analogous nanostructures of similar geometry as described above are farther contemplated for use in elastomer seals of the present disclosure. For example, the boron analogs of fullerenes recently described by researchers at

Rice University, Houston, Tex. fall within the spectrum of nanomaterial additives contemplated as a nanomaterial additive to the elastomer seal.

**[0071]** Nanodiamonds

**[0072]** In particular embodiments, the at least one nanomaterial additive may include diamond particles or diamond-like particles. One suitable method for generating nanodiamonds may include, for example, a detonation process as described in *Diamond and Related Materials* (1993, 160-2), which is incorporated by reference in its entirety, although nanodiamonds produced by other methods may be used. Those having ordinary skill in the art will appreciate how to form nanodiamond particles. Briefly, in order to produce nanodiamond by detonation, detonation of mixed high explosives in the presence of ultradispersed carbon condensate forms ultradispersive diamond-graphite powder (diamond blend or DB), which is a black powder containing 40-60 weight percent of pure diamond. Chemical purification of DB generates pure nanodiamond (ultradispersive detonational diamond or UDD), a grey powder containing up to 99.5 weight percent of pure diamond. The ultrafine diamond particles generated by the detonation process may comprise a nanodiamond core, a graphite inner coating around the core, and an amorphous carbon outer coating about the graphite. Both the graphite coating and amorphous carbon coating may be optionally removed by chemical etching. In some embodiments, the nanodiamond particles may be clustered in loose agglomerates ranging in size from nanoscale to larger than nanoscale. Diamond or diamond-like particles may be added to elastomer seals disclosed herein in an amount greater than about 0.1, 0.2, 0.5 volume percent in some embodiments, and less than 10, 5, 2, and 1 volume percent in other embodiments.

**[0073]** In particular embodiments, the nanomaterial additive may include at least one of an inorganic nanomaterial, such as a metal oxide nanoparticle. One suitable method for generating metal oxide nanoparticles is by using plasma synthesis, although metal oxide nanoparticles produced by other methods may be used. Those having ordinary skill in the art will appreciate how to form metal oxide nanoparticles. Metal oxide nanoparticles may comprise oxides of zinc, iron, titanium, magnesium, silicon, aluminium, cerium, zirconium, mixed metal compounds or mixtures thereof. Further, other nanoparticles such as nanopowders, inorganic nanoparticles such as calcium carbonate, nanofibers, and a mixture of nanomaterials can be used in elastomer seals of the present disclosure.

**[0074]** Integration of the nanomaterial additive into the elastomer seal may include any means as known to those skilled in the art. As used herein, integration refers to any means for adding the nanomaterial additive to a component of the elastomer seal such that the nanomaterial additive is a component of the formed elastomer seal, i.e., by exfoliation, hot-melting, plastic extrusion, or other forms of incorporation of the nanomaterial additive as known to those skilled in the art. In some embodiments, the nanomaterial additives may be integrated in such a manner so as to achieve a generally uniform dispersion of the nanomaterial additives through the formed composite body.

**[0075]** For example, nanomaterial additives may be integrated with the elastomer composition prior to curing. These nanomaterial additives may be added, compounded, or blended with the elastomer seal precursors, prior to the curing process. For instance, the base elastomer may be compounded or mixed with additives or agents such as furnace black, peroxide curing agent, graphite, zinc oxide, stearic acid, plasticizer, and nanomaterial additives. Alternatively, the nanomaterial may be integrated into the elastomer seal post-cure by methods such as spraying, hot melting, plastic extrusion, and other methods known in the art.

**[0076]** Advantageously, embodiments of the present disclosure contain elastomer seal containing nanomaterial additives, which may confer superior properties such as enhanced elastic and tensile moduli, hardness, and tear strength. These enhanced properties would allow the seal to withstand the harsh conditions of elevated temperatures, pressures, and constant friction for longer periods of time. This may prolong the downhole life of the nanocomposite elastomer seal and ultimately the rock bit. This seal life extension would serve to significantly reduce drilling downtime, and be invaluable in the oil and gas industry.

**[0077]** While the present disclosure has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments may be devised which do not depart from the scope of the present disclosure as disclosed herein. Accordingly, the scope of the present disclosure should be limited only by the attached claims.

What is claimed;

**1**. A bit for drilling subterranean formations comprising:
a bit body including a bearing surface;
a cutting structure mounted on the bit body, and including a bearing surface; and
an annular seal for retaining a grease between the bearing surfaces, the annular seal comprising a flexible and resilient seal body formed from an elastomer composition, wherein the elastomer composition comprises an elastomer material, a curing agent, and 10% or less by volume of a nanomaterial additive selected from one of nanotubes and clustered nanodiamonds.

**2**. The bit of claim **1**, wherein the elastomer material comprises at least one of a highly saturated nitrile elastomer, a nitrile-butadiene rubber, a highly saturated nitrile-butadiene rubber, a fluorocarbon, an ethylene-propylene, a silicone, a chloroprene, a neoprene, a fluorosilicone, a polyurethane, a perfluoroelastomer, a polyacrylate, a copolymer of tetrafluoroethylene and propylene, an ethylene-acrylic rubber, a chlorosulfonyl polyethylene rubber, an epichlorohydrin polymers, a styrene butadiene polymer, and mixtures or copolymers thereof.

**3**. The bit of claim **1**, wherein the curing agent, comprises at least one of an organometallic catalyst, an inorganic oxide, an inorganic peroxide, a metal oxide salt, an organic peroxide, an organic hydroperoxide, and mixtures thereof.

**4**. The bit of claim **1**, wherein the nanomaterial additive comprises a functionalized nanotube.

**5**. The bit of claim **1**, wherein the elastomer composition comprises 0.01 to 1.5% by volume of nanomaterial additives.

**6**. The bit of claim **1**, wherein the elastomer composition comprises from about 2 to 4% by volume of nanomaterial additives.

**7**. The bit of claim **1**, further comprising an additive which is at least one of a coagent, a plasticizer, a lubricant, an antioxidant, a filler, an accelerator, and a retardant.

**8**. The bit of claim **7**, wherein the plasticizer comprises at least one of a phthalate, a chlorinated paraffin, an adipate, a trimellitate, a maleate, a sebacate, a benzoate, an epoxidated vegetable oil, sulfonamides, an organophosphate, a glycol and a polyether.

**9**. The bit of claim **7**, wherein the lubricant comprises at least one of a graphite, an oleamide, an erucarnide, a soy oil, waxes, or a mixture of blend thereof.

**10**. The bit of claim **7**, wherein the antioxidant comprises at least one of zinc 2-mercaptotolumimidazole, 4,4'-Bis(alpha, alpha-dimethylbenzyl) diphenylamine.

**11**. The bit of claim **7**, where the filler comprises at least one of a calcium carbonate, a carbon black, a titanium dioxide, a non-acidic clay, a fumed silica, a metal oxide, a metal chromate, a metal sulfate, and a mixture thereof.

**12**. The bit of claim **7**, wherein the accelerator comprises at least one of an amine, a sulfonamide, and a disulfide.

**13**. The bit of claim **7**, wherein the retardant comprises least one of a stearate, an organic carbamate and salts thereof, a lactone, and a stearic acid.

**14**. A rock bit for drilling subterranean formations comprising:

a bit body including at least one journal pin, each having a bearing surface;

a roller cone mounted on the at least one journal pin and including a bearing surface;

an annular seal for retaining a grease between the bearing surfaces, the annular seal comprising a flexible and resilient seal body formed from an elastomer composition, wherein the elastomer composition comprises;

100 parts by weight of highly saturated nitrile elastomer;

furnace black in the range of up to 70 parts by weight;

peroxide curing agent in the range of from 7 to 10 parts by weight;

zinc oxide in the range of from 4 to 7 parts by weight;

stearic acid in the range of from 0.5 to 2 parts by weight;

nanomaterial additives selected from one of nanotubes and clustered nanodiamonds in the range of up to 10 percent by volume, and sufficient plasticizer to provide a Shore Hardness of no more than A 80.

**15**. The rock bit of claim **14**, wherein the nanoadditive materials comprises functionalized nanotubes.

**16**. The rock bit of claim **14**, wherein the elastomer composition comprises 0.01 to 1.5% by volume of nanomaterial additives.

**17**. The rock bit of claim **14**, wherein the plasticizer comprises at least one of a phthalate, a chlorinated paraffin, an adipate, a trimellitate, a maleate, a sebacate, a benzoate, an epoxidated vegetable oil, sulfonamides, an organophosphate, a glycol and a polyether.

**18**. The rock bit of claim **14**, further comprising an additive which is at least one of a coagent, an antioxidant, and an accelerator.

**19**. The rock bit of claim **18**, wherein the coagent is at least one of polybutadiene. The rock bit of claim **18**, wherein the antioxidant comprises at least one of zinc 2-mercaptotolumimidazole, 4,4'-Bis(alpha,alpha-dimethylbenzyl) diphenylamine.

**20**. The rock bit of claim **18**, wherein the accelerator comprises at least one of an amine, a sulfonamide, and a disulfide.

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