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(54) **HIGHLY POROUS COOLANT CONDITIONING AND REMEDIATION MEDIA**

(71) Applicants: **Matthew Hobbs**, Calgary, CA (US); **Peter T Dufresne**, Calgary (CA)

(72) Inventors: **Matthew Hobbs**, Calgary, CA (US); **Peter T Dufresne**, Calgary (CA)

(73) Assignee: **1441413 Alberta Inc. DBA EPT**, Calgary (CA)

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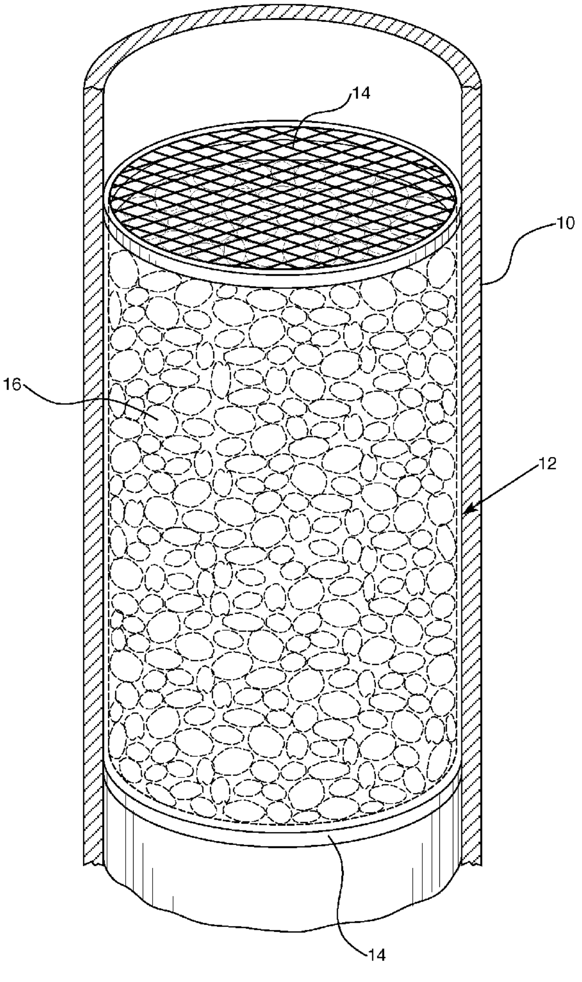
(57) **ABSTRACT**

The present invention is a solid cooling fluid treatment medium, usually but not always in bead form, suitable to be brought into contact with coolants to remediate and to condition them. A key feature of the medium, typically a polymeric resin, is the presence of relatively very large pores, which are able to capture and remove ultrafine coolant contaminants and breakdown products (such as colloids, soot, coke, organics, scale or other small semi-soluble or insoluble particles). Resins and adsorbents of the prior art have proven unable to remove ultrafine contaminants like these that have a deleterious impact on industrial equipment performance and reliability. The mean pore size diameter of the medium is between about 1,500 Å and 100,000 Å and, more preferably, in the range of about 1,500 Å to about 80,000 Å.



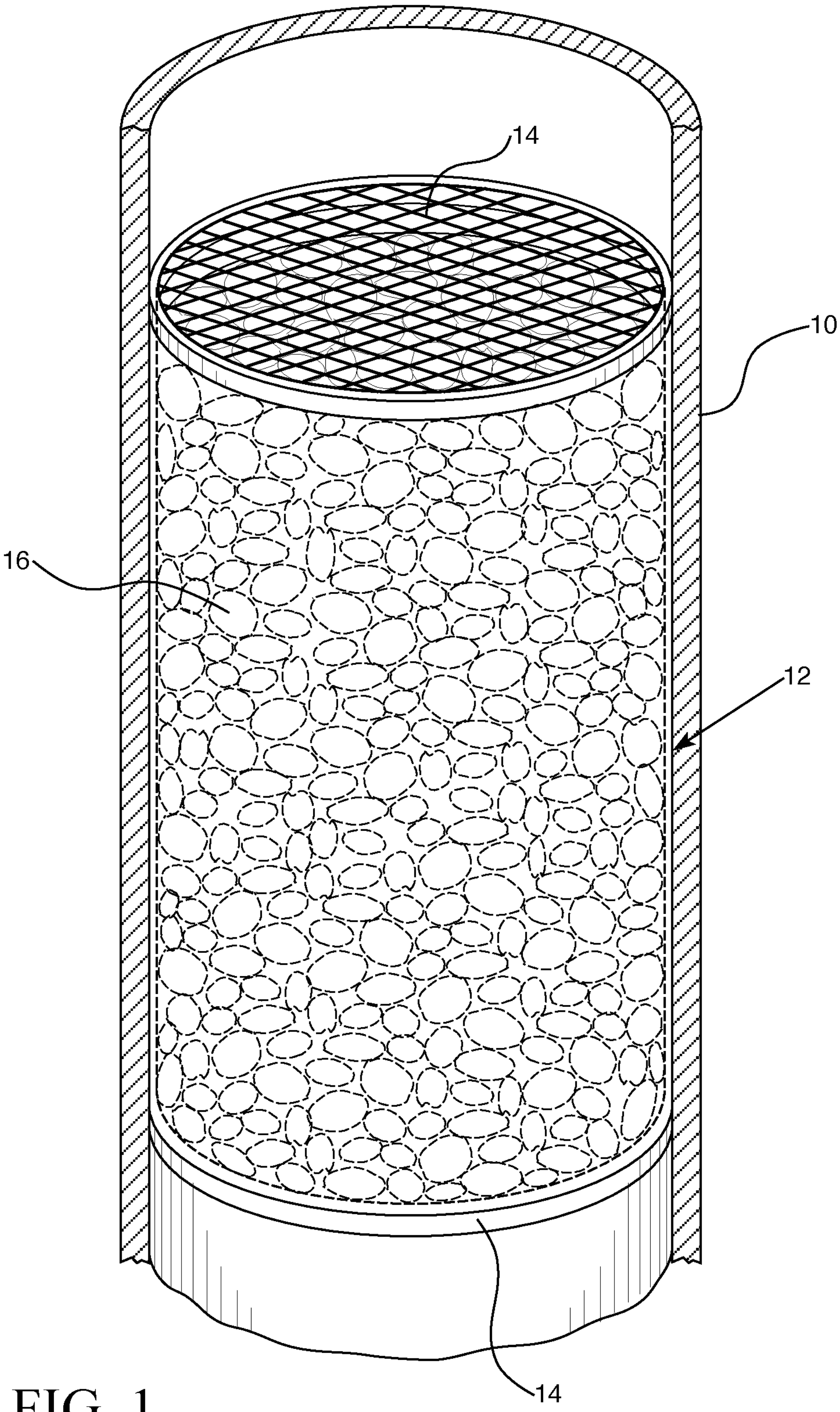


FIG. 1

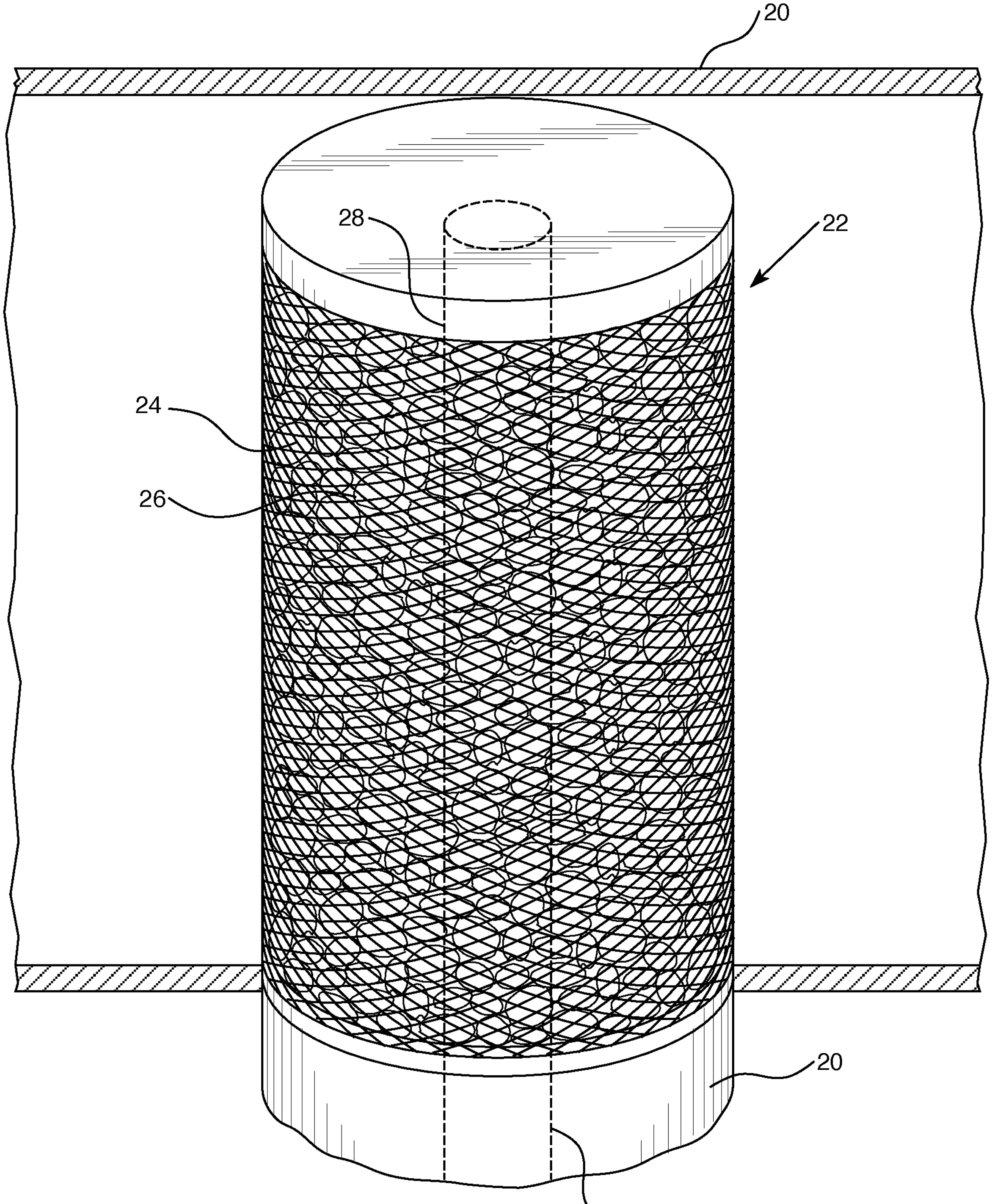


FIG. 2

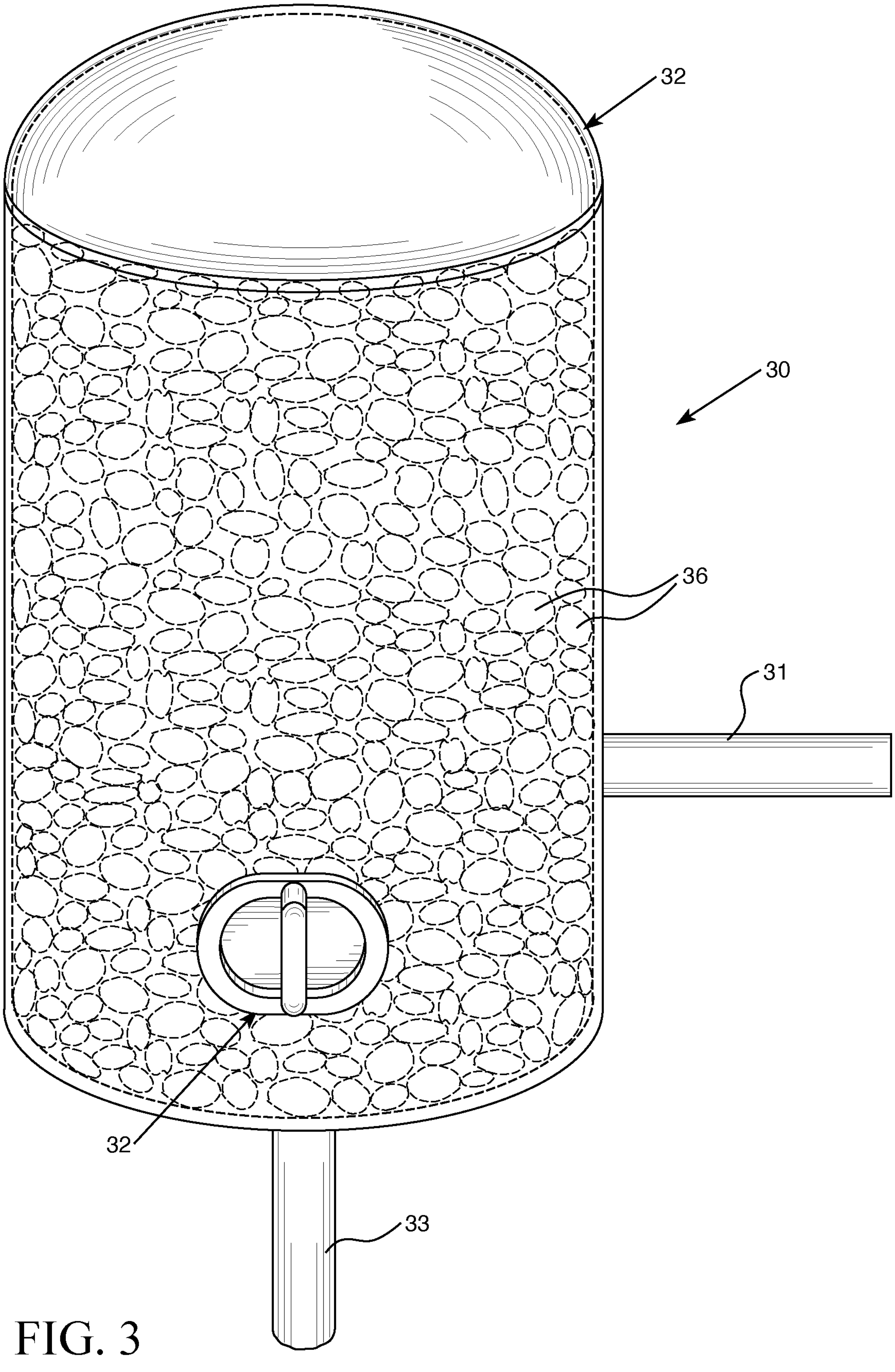


FIG. 3

HIGHLY POROUS COOLANT CONDITIONING AND REMEDIATION MEDIA

[0001] This patent application claims priority to, and incorporates herein by reference. U.S. Provisional Application for Pat. No. 62/718,638, filed 14 Aug. 2018.

FIELD OF THE INVENTION

[0002] The present invention is a solid and unusually porous medium for use in conditioning or remediating industrial cooling fluids such as glycol(s) used in antifreeze or heat exchange applications.

BACKGROUND OF THE INVENTION

[0003] The efficient and reliable operation of critical industrial equipment relies upon the use of coolants or other functional fluids. Industrial coolants (including water/glycol-based cooling fluids), however, are subject to degradation and contamination during service. This often leads to an accumulation of metals, corrosive species and ultrafine erosive particles, impairing the coolant's ability to fulfill its duties effectively. These cooling fluids must, therefore, be maintained in acceptable condition to ensure that critical equipment performs reliably. When cooling fluids are not kept in acceptable condition, costly equipment failure and downtime may result. Successful maintenance strategies must, therefore, provide a means of identifying and addressing the accumulation of deleterious coolant contaminants and degradation products that occurs during service. Coolant analysis and a variety of filtration or conditioning systems are generally used to monitor and maintain coolant condition, respectively.

[0004] Contamination and degradation during coolant service is inevitable. Insoluble particles (including ultrafine erosive colloids), corrosive species and metals are common contaminants in aqueous or pure glycol-based cooling fluids and their deleterious impact on equipment performance and reliability is well-established.

[0005] Because of their effect on equipment reliability and performance, cooling fluid contaminant and degradation levels are generally monitored using coolant analysis. Common test methods include (but are not limited to): metal levels, anion chromatography for corrosives, pH analysis, glycol content and evaluation of coolant color/appearance. The latter test can be used to subjectively gauge the level of erosive ultrafine solids that have accumulated. Objective measurement of these ultrafine colloids can also be accomplished by visible absorption spectroscopy, however, this methodology is not widely employed. Many operators, therefore, have no basis for trending the presence of erosive ultrafines in their cooling fluids.

[0006] After deleterious cooling fluid contaminants and degradation products have been identified by coolant analysis, they must be addressed by filtration or conditioning systems to ensure that critical equipment performs as intended. In this regard, prior art includes mechanical filtration systems, adsorbents and treatment systems employing solid ion exchange media of, relatively, limited porosity. The latter are used to remove acidic degradation products, corrosive species and metals from glycol-based cooling fluids and their utility in this regard is explored in Wiebe, René D. "Ion-Exchange Coolant Recycling Meets ASTM Proposed Specifications." *SAE Transactions* 103 (1994): 823-44. These resins contain relatively small pores to increase the solid media's surface area available for ion exchange. Coolant metal and corrosive anion levels have been effectively managed for many years using the above discussed prior art. Ultrafine erosive solids cannot, however, be effectively addressed using these previously disclosed technologies. Through the use of visible absorption spectroscopy, the extent of coolant colloid/ultrafine problems has become obvious and the root cause of many costly industrial failures has been linked to these contaminants. Prior to the present invention, a need, therefore, remained to develop coolant filtration, treatment or conditioning systems able to remove harmful ultrafine colloids from glycol-based cooling fluids and analogous contaminants from other industrial fluids of a generally similar nature.

SUMMARY OF THE INVENTION

[0007] In order to meet this need, the present invention is a cooling fluid filtration and conditioning system which uses ion exchange resin or a mixture of ion exchange resins in which the pore size of at least some of the resin is significantly (on the order of two times or more) greater than the pores of prior art filters and resins. The use of ion exchange resins featuring unusually large pores was, heretofore, counterintuitive since their large pore volume limits the surface area available for ion exchange/contaminant-removal. As a result, the ion exchange resins of the present invention are relatively inefficient acid, anion and metal scavengers relative to those of the prior art. The inventive ion exchange resins featuring unusually large pore sizes are, however, surprisingly able to capture and retain extremely fine (smaller than 1-4 μm in diameter) particles (including erosive colloids) from coolants. The ion exchange resin's unusually large pores may also be able to capture and retain ultrafine soot, coke, organic or scale particles. Moreover, the highly porous ion exchange resins of the present invention can capture, retain and remove these fine insoluble contaminants and breakdown products (colloids, soot, coke, organics, scale etc.) in a way that conventional mechanical filtration media having the same interstitial dimensions (1-4 μm, for instance) cannot. On this basis, the present large-pore ion exchange resins do not appear to function as simple sieves. This suggests that the three-dimensionally highly porous structure of the polymer ion exchange resin medium plays a significant role in the efficient capture and retention of fine insoluble coolant contaminants and breakdown products. By using the present invention, the risk of cooling fluid condition-related costly industrial equipment failures can be effectively mitigated.

[0008] More particularly, the present invention comprises an unusually porous ion exchange resin for use in cooling fluid remediation and conditioning. The unusually porous ion exchange resins of the present invention typically take the form of macroporous polymer beads having a bead size of 300-1,500 μm. The cooling fluid is brought into contact with the inventive ion exchange resins either during cleaning periods or while the fluid is in-service. The pores of the present ion exchange resins are on the order of two times or more larger than the typical median pore sizes of ion exchange resins already known in the art (as measured by mercury porosimetry). For example, typical prior art resin beads have median pore sizes of on the order of 400-900 Å, whereas the present invention large-pore ion exchange resins have median pore sizes beginning on the order of 1500

Å and up to 40,000 Å or even up to 60,000-100,000 Å. The inventors also believe that ion exchange resins featuring a median pore size between 1500-100,000 Å will give new and unexpectedly improved coolant contaminant and breakdown product removal results compared with resins having smaller (or, ostensibly, larger) pores than those within that stated range.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. **1**. is a sectional view of an array configured for axial flow.

[0010] FIG. **2**. is a sectional view of an array configured for radial flow.

[0011] FIG. **3** is a plan view of a bulk treatment vessel containing the present medium, with an inlet and outlet for fluid flow.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present inventive ion exchange resins feature unusually large pore sizes, allowing for the, heretofore, impossible capture of fine coolant contaminants and breakdown products (colloids, soot, coke, organics, scale etc.). These contaminants and degradation products are typically less than 1-4 μm in size and, therefore, difficult or impossible to remove via sieve-type techniques described within the prior art. By using ion exchange resins with pore sizes on the order of two times or more greater than those described throughout the prior art, the present inventive resins allow for the efficient removal of ultrafine coolant contaminants and breakdown products. These deleterious species enter the relatively larger pores of the inventive ion exchange resins where they are then captured and retained. Typical polymer resins meant for use in the present invention are (without limitation): polystyrene (including cross-linked polystyrenes), polyurethane, epoxy, polyvinyl, vinyl ester, divinylbenzene or acrylic resins of virtually any type as long as they are polymers in the generally understood plastic family. These polymeric resins may be functionalized to form anionic or cationic exchange resins or the polymer may remain unfunctionalized. The use of functionalized anion or cation exchange resins may, however, enhance the solid medium's ability to remove other undesirable contaminants and breakdown products (acids, metals, corrosive anions etc.) from coolants.

[0013] Given the above explanation of how the "larger pore" inventive resins capture ultrafine insoluble coolant colloid particles etc., the inventors' motivations for employing the unusually porous inventive resins might seem apparent. The use of these relatively large pore-containing ion exchange resins was, however, utterly counterintuitive. Since the ion exchange resins described in the prior art are intended to remove corrosive anions, acids and dissolved metal contaminants, one skilled in the art of coolant treatment would select a resin having a high exchange (acid/metal/anion-removal) capacity. Ion exchange resins with many, smaller pores feature more surface area and, therefore, offer inherently greater contaminant-removal abilities. Intuitively, one skilled in the art of coolant treatment would also select an ion exchange resin with smaller pores and greater surface area to maximize the treatment medium's adsorbing/exchange capacity. By drastically increasing the median pore sizes in the present ion exchange resins, the inventors have acted in complete contradiction with this established wisdom, and have accordingly, overwhelmingly, reduced the inventive ion exchange resin's surface areas. This counterintuitive significant (on the order of two times or more) increase in ion exchange resin pore size has, nevertheless, led to novel and surprisingly improved results to treat the, heretofore, unappreciated and unresolved problem of ultrafine, erosive coolant contaminants and breakdown products (colloids, soot, coke, organics, scale etc.).

[0014] The present invention focuses on the, heretofore, difficult or impossible removal of ultrafine cooling fluid contaminants and breakdown products (colloids, soot, coke, organics, scale etc.) at the expense of the inventive media's acid/metal/anion-removal capabilities. The prior art necessity of contaminant-removal, however, remains important. Fortunately, it is possible to functionalize the present larger-pore ion exchange resins with chemical moieties to address these contaminants. It is equally feasible to combine the present larger-pore ion exchange resins (be they functionalized or not) with other ion exchange resins whose pore sizes are smaller and contaminant-removal capacities are concomitantly greater. This combination of inventive ion exchange resin with more conventional prior art resins may be accomplished by mixing or layering two or more types of ion exchange resin beads. It is generally desirable to combine about 75% (w/w) of the inventive "large-pore" ion exchange resins with about 25% (w/w) of the traditional ion exchange resins; it is equally tenable that the mixture or layering can be about 50% of each. After one understands the different mechanisms by which the inventive and prior art ion exchange resins work (as described herein), the choice of ratio has to do with the need for anion/metal-removal vs. ultrafine-removal primarily since a reduction in the amount of traditional anion/metal media stoichiometrically reduces the overall ion exchange resin mixture's contaminant-removal capacity concomitantly. As to the inventive ion exchange resins, an inclusion of approximately 75% has been shown to allow for the efficient capture of significant amounts of ultrafine coolant contaminants and breakdown products.

[0015] One skilled in the art of coolant-conditioning and ion exchange will recognize the need to maintain coolant pH within a desirable, very slightly alkaline range (generally pH=8.0-10.5). It is, therefore, imperative that if anionic or cationic forms of the inventive resins are used, that these be balanced by the use of a stoichiometric quantity of resin of the opposite type. If inventive highly porous anion resins are used, this, therefore, requires the complimentary use of cation resin to maintain coolant pH. If inventive highly porous cation resins are used, this, therefore, requires the complimentary use of anion resin to maintain coolant pH. In situations where coolant pH is outside of the desired range, one skilled in the art will be able to modify the ratio of cation/anion resin in such a way as to ensure that coolant pH is restored to the desirable, slightly alkaline range. The combination of anion and cation resins can be achieved by mixing or layering the different resin types. It is equally feasible to treat the cooling fluids of interest with a column/cartridge containing one resin type (anion for instance) followed by a separate column/cartridge containing the complimentary resin type (cation in this instance).

[0016] Clearly, then, the inventive core is the insight into using ion exchange resins having relatively larger (on the order of two times or more) pores to trap ultrafine coolant contaminants and breakdown products including colloids, soot, coke, organics, scale (which have, heretofore, not been adequately quantified and trended but, nevertheless, led to avoidable equipment failures, downtime and premature cooling fluid replacement).

[0017] Referring now to FIG. **1**, a sectional view of a portion of pipe **10** typical of a cleaning loop in a coolant system is shown in section with a cartridge **12** in place. The cartridge **12** is a section of the pipe in which two barriers **14**, typically a pored screen or mesh, are positioned both upstream and downstream of a quantity of porous beads **16** of solid medium according to the invention. The beads are enlarged in the Figure for illustration purposes and therefore are not shown to scale. The pores or mesh screen holes in the barrier **14** need only to be smaller than the smallest size of the beads **16** to hold them in their position within the cartridge **12**. The cartridge **12** can be removed, for replacement of the beads **16**, via threaded fasteners **18** or an equivalent means of structural integrity including press-fit, epoxy sealing, welding, robotic sealing or any other means of construction. One or more traditional particulate filters (not shown) can be added at any point along the fluid flow, and are optional. The section of pipe **10** can be placed in any convenient location in a coolant system, preferably in a location of easy access for maintenance (replacement of the solid medium beads). Although not shown in FIG. **1**, it is also beneficial to introduce a "kidney loop" format secondary to a primary filtration system or as part of a primary circulation system, especially for coolant remediation. FIG. **2** shows an alternative configuration for radial flow, with the cartridge **22**, barrier **24**, beads **26**, an inlet pipe **20** and an outlet pipe **28**, all analogous to FIG. **1**. FIG. **3** is a plan view of a bulk treatment alternative, in which a vessel **30** holds the beads **36** of the present invention, which can be charged to the container via hatch **32**, with the fluid flow entering via pipe **31** and exiting via pipe **33**. The vessel contains an optional domed lid hatch **32** which can be used as an alternate access point for adding or removing the present beads. Again, in none of these Figures are the beads shown to scale.

[0018] It should be understood that the configuration of FIG. **1** is not shown to scale. Cooling fluid applications can contain from 400 to 200,000 gallons of coolant, typically, or even less or more than that, and the associated media needed according to the invention increases or decreases proportionately. The amount of media needed also varies as a function of the condition of the fluid to be treated. Fluids containing very high levels of contaminants will require concomitantly more media. The types of coolants that can be conditioned or remediated in the present invention (with or without the specific structures shown in FIG. **1**) are glycol-based cooling fluids and aqueous mixtures of glycol-based cooling fluids. The present invention, therefore, accommodates a wide variety of media amounts and fluid systems, and those skilled in the art learning from this specification to use the disclosed media with relatively much larger pores will easily be able, without undue experimentation, to determine how much porous resin media to use and how often to replace it. Having said that, a typical installation for a 50:50 water/ethylene glycol system could include, without limitation, two cartridges 1 foot in diameter each and 20 inches in length containing the beads of the present disclosure (any of the 100% inventive beads, 50% inventive beads and 50% prior art beads or other media beads, or the above-described 75% inventive beads and 25% prior art or other media beads) to treat about 6,000 gallons of coolant.

[0019] Although the invention has been described with particularity above, the invention is only to be limited insofar as set forth in the accompanying claims.

We claim:

1. A polymer resin medium for use in conditioning or remediating a cooling fluid, in which a quantity of polymer resin contains a plurality of pores and further wherein said pores have a mean diameter of between 1,500 and 100,000 Å as measured by mercury porosimetry.

2. The polymer resin medium according to claim **1**, wherein said pores have a mean diameter of between 20,000 and 80,000 Å as measured by mercury porosimetry.

3. The polymer resin medium according to claim **1**, wherein said polymer resin is selected from the group consisting of polystyrene, cross-linked polystyrene, polyurethane, epoxy, polyvinyl, vinyl ester, divinylbenzene or acrylic materials.

4. The polymer resin medium according to claim **1**, wherein said pores have a mean diameter of between 8,000 and 60,000 Å as measured by mercury porosimetry.

5. The polymer resin medium according to claim **1** wherein said polymer resin is in the form of beads.

6. The polymer resin medium according to claim **5** wherein said beads have a mean diameter of between about 100-2,000 μm.

7. The polymer resin medium according to claim **6** wherein said beads are suitable for mixing, admixing or layering with other media beads for treatment of cooling fluids.

8. A method of cleaning a quantity of cooling fluid, comprising contacting all or a portion of the coolant to be cleaned with a quantity of polymer medium having pores distributed throughout, wherein ultrafine and colloidal coolant contaminants and breakdown products smaller than 4 μm are captured by said pores, said pores' further having a mean diameter of between 1,500 Å and 100,000 Å as measured by mercury porosimetry.

9. The method of claim **8**, wherein said polymer medium is in the form of beads.

10. The method of claim **8**, wherein said polymer medium is selected from the group consisting of polystyrene, cross-linked polystyrene, polyurethane, epoxy, polyvinyl, vinyl ester, divinylbenzene, and acrylic.

11. The method of claim **8**, wherein the absorbance of a water-glycol-based cooling fluid can be significantly improved to a value of<0.1000.

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