

**Chapter 1 : Energy harvesting - Wikipedia**

*The main scavenging methods are cross scavenging, loop scavenging and uniflow scavenging. The gas exchange process in two-stroke engines can be characterized with a number of parameters including delivery ratio, scavenge ratio, scavenge efficiency, purity of charge and trapping efficiency.*

Smart roads have the potential to play an important role in power generation. Embedding piezoelectric material in the road can convert pressure exerted by moving vehicles into voltage and current. Piezoelectric sensors are most useful in Smart-road technologies that can be used to create systems that are intelligent and improve productivity in the long run. Imagine highways that alert motorists of a traffic jam before it forms. Or bridges that report when they are at risk of collapse, or an electric grid that fixes itself when blackouts hit. For many decades, scientists and experts have argued that the best way to fight congestion is intelligent transportation systems, such as roadside sensors to measure traffic and synchronized traffic lights to control the flow of vehicles. But the spread of these technologies has been limited by cost. There are also some other smart-technology shovel ready projects which could be deployed fairly quickly, but most of the technologies are still at the development stage and might not be practically available for five years or more. It is analogous to the piezoelectric effect, which is another type of ferroelectric behavior. Pyroelectricity requires time-varying inputs and suffers from small power outputs in energy harvesting applications due to its low operating frequencies. One way to directly convert waste heat into electricity is by executing the Olsen cycle on pyroelectric materials. The Olsen cycle consists of two isothermal and two isoelectric field processes in the electric displacement-electric field D-E diagram. The principle of the Olsen cycle is to charge a capacitor via cooling under low electric field and to discharge it under heating at higher electric field. Several pyroelectric converters have been developed to implement the Olsen cycle using conduction, [50] convection, [51] [52] [53] [54] or radiation. Additionally, a pyroelectric scavenging device that does not require time-varying inputs was recently introduced. The energy-harvesting device uses the edge-depolarizing electric field of a heated pyroelectric to convert heat energy into mechanical energy instead of drawing electric current off two plates attached to the crystal-faces. Thermoelectric generator In , Thomas Johann Seebeck discovered that a thermal gradient formed between two dissimilar conductors produces a voltage. At the heart of the thermoelectric effect is the fact that a temperature gradient in a conducting material results in heat flow; this results in the diffusion of charge carriers. The flow of charge carriers between the hot and cold regions in turn creates a voltage difference. In , Jean Charles Athanase Peltier discovered that running an electric current through the junction of two dissimilar conductors could, depending on the direction of the current, cause it to act as a heater or cooler. The heat absorbed or produced is proportional to the current, and the proportionality constant is known as the Peltier coefficient. Today, due to knowledge of the Seebeck and Peltier effects, thermoelectric materials can be used as heaters, coolers and generators TEGs. Ideal thermoelectric materials have a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. Low thermal conductivity is necessary to maintain a high thermal gradient at the junction. Standard thermoelectric modules manufactured today consist of P- and N-doped bismuth-telluride semiconductors sandwiched between two metallized ceramic plates. The ceramic plates add rigidity and electrical insulation to the system. The semiconductors are connected electrically in series and thermally in parallel. Practical examples are the finger-thermometer by the Holst Centre and the thermogenerators by the Fraunhofer Gesellschaft. No moving parts allow continuous operation for many years. Tellurex Corporation [62] a thermoelectric production company claims that thermoelectrics are capable of over , hours of steady state operation. Thermoelectrics contain no materials that must be replenished. Heating and cooling can be reversed. The development of materials that are able to operate in higher temperature gradients, and that can conduct electricity well without also conducting heat something that was until recently thought impossible[ citation needed ], will result in increased efficiency. Future work in thermoelectrics could be to convert wasted heat, such as in automobile engine combustion, into electricity. Vibrations separate the plates of a charged variable capacitor, and mechanical energy is converted into electrical energy. Electrostatic energy harvesters need a

polarization source to work and to convert mechanical energy from vibrations into electricity. The polarization source should be in the order of some hundreds of volts; this greatly complicates the power management circuit. Another solution consists in using electrets, that are electrically charged dielectrics able to keep the polarization on the capacitor for years. By developing a miniature device of this kind in [1], a team from the University of Southampton made possible the planting of such a device in environments that preclude having any electrical connection to the outside world. Sensors in inaccessible places can now generate their own power and transmit data to outside receivers. Further reductions in the dimensions are possible through the integration of new and more flexible materials as the cantilever beam component. In [2], a group at Northwestern University developed a vibration-powered generator out of polymer in the form of a spring. A new approach to magnetic induction based energy harvesting has also been proposed by using ferrofluids. The journal article, "Electromagnetic ferrofluid-based energy harvester", discusses the use of ferrofluids to harvest low frequency vibrational energy at [2]. Another example is the products developed from the early University of Southampton prototypes by Perpetuum. These have to be sufficiently large to generate the power required by wireless sensor nodes wsn but in M2M applications this is not normally an issue. Overhead powerline sensors can use magnetic induction to harvest energy directly from the conductor they are monitoring. These energy harvesters are called biobatteries. They could be used to power implanted electronic devices e. At present, the Minteer Group of Saint Louis University has created enzymes that could be used to generate power from blood sugars. However, the enzymes would still need to be replaced after a few years. Voltree has developed a method for harvesting energy from trees. These energy harvesters are being used to power remote sensors and mesh networks as the basis for a long term deployment system to monitor forest fires and weather in the forest. A small test network was recently deployed in a US National Park forest. Theoretical analysis of this source of energy shows some promise in powering small electronic devices. The device can be tuned to harvest other signals including Wi-Fi signals, satellite signals, or even sound signals. The experimental device used a series of five fiberglass and copper conductors. Conversion efficiency reached 37 percent. When traditional antennas are close to each other in space they interfere with each other. While the claim of [7]. Since the power is so low, there can be almost no current when any load is attached. Atmospheric pressure changes[ edit ] The change in air pressure due to temperature changes or weather patterns vs. What is an Atmospheric pressure change? An Atmospheric change is a force exerted on a surface by air above as gravity pulls it to Earth. This is often measured by the barometer, a slight mercury in the glass tube rises and drops depending on changes in altitude and pressure. Usually, atmosphere pressure drops as altitude increases, also vice versa. Overall an Atmospheric pressure is a great utility that can be devised into our economy for top-tier energy harvest and future solution for many other issues [80]. Ocean Energy[ edit ] A relatively new concept of generating energy is to generate energy from oceans. Large masses of waters are present on the planet which carry with them great amounts of energy. The energy in this case can be generated by tidal streams, ocean waves, difference in salinity and also difference in temperature. Efforts are underway to harvest energy this way as it holds a great potential and would be a renewable form of energy. United States Navy recently was able to generate electricity using difference in temperatures present in the ocean. Another idea is to generate an artificial flow in ocean to generate energy. If a flow of considerable magnitude could be generated it would produce large amounts of energy. Future directions[ edit ] Electroactive polymers EAPs have been proposed for harvesting energy. These polymers have a large strain, elastic energy density, and high energy conversion efficiency. The total weight of systems based on EAPs electroactive polymers is proposed to be significantly lower than those based on piezoelectric materials. Nanogenerators, such as the one made by Georgia Tech, could provide a new way for powering devices without batteries. Noise has been the subject of a proposal by NiPS Laboratory in Italy to harvest wide spectrum low scale vibrations via a nonlinear dynamical mechanism that can improve harvester efficiency up to a factor 4 compared to traditional linear harvesters. This type of complementary balanced energy harvesting has the potential to increase reliability of wireless sensor systems for structural health monitoring.

**Chapter 2 : USA - Method of scavenging hydrogen sulfide - Google Patents**

*The 37Å°C 70% ethanol extract of seasoned laver had more powerful inhibitory effects for ABTS radical scavenging than other extraction methods across all laver products. In addition, 37Å°C 70% ethanol extracts had the highest superoxide radical scavenging capacities and hydroxyl radical scavenging activities.*

The treatment of water for use in steam generating equipment is a very critical and complex art due to the numerous sources of scaling, corrosion and other water related problems typically encountered in operating such equipment. This invention is concerned with a method of conditioning feedwater to protect preboiler, boiler and condensate systems of steam generating equipment against corrosion during operation and lay-up. The most common source of corrosion in such systems is oxygen attack of steel components. Unfortunately, oxygen attack of steel is accelerated by the unavoidably high temperatures found in boiler equipment. Also, if boiler water pH is permitted to become acidic which helps control scale formation, oxygen attack is yet further accelerated. In most modern steam generating systems, dissolved oxygen levels are controlled by first mechanically removing the bulk of the dissolved oxygen and then chemically scavenging the remainder. Mechanical degasification is typically carried out with vacuum degasifiers which reduce oxygen levels to less than 0. Traditionally, sodium sulfite and hydrazine have been used to chemically scavenge the oxygen remaining in steam generating systems after the initial mechanical removal of the bulk of the dissolved oxygen. Each of these traditional treatments has significant shortcomings. Sodium sulfite, for example, is not recommended for use in systems operating above psi because corrosive hydrogen sulfide and sulfur dioxide can be formed at pressures above this point. Also, sodium sulfite can contribute to increased dissolved solids in the feedwater, requiring higher boiler blowdown rates and, therefore, higher water, fuel and chemical costs. Hydrazine is less effective than sulfite in removing oxygen. However, since hydrazine also acts as a corrosion inhibitor by maintaining a passive, protective film on system components, it is an effective alternative to sulfite. Unfortunately, though, hydrazine is a toxic substance which must be handled with extreme care in all applications. Indeed, Food and Drug Administration rules prohibit the presence of measurable quantities of hydrazine in any applications in which it might come in contact with food. It is, therefore, an object of the present invention to provide an improved method for scavenging oxygen in steam generating systems which relies on neither sulfite nor hydrazine. It is a further object of the present invention to provide a feedwater conditioning method for passivating metal surfaces in steam generating equipment without relying on hydrazine. Other objects and advantages of the present invention will become apparent from the discussion below. Useful amine salts include the erythorbates of morpholine, cyclohexylamine, diethanolamine and triethanolamine. The ammonium neutralized erythorbate is the most preferred agent. Ammonium neutralized erythorbate is the most preferred agent because it does not contribute to system solids levels and because it can be formulated in concentrates at up to a 25 percent by weight actives level. Furthermore, the ammonium form has been found to react faster with oxygen at higher temperatures than the corresponding sodium salt Example 3 below. The key parameters governing the effectiveness of an oxygen scavenging agent are its reactivity with oxygen, with metal surfaces, and with feedwater contaminants. These parameters are dependent upon both temperature and chemical concentrations. The scavenging agents of the present invention are effective oxygen scavengers over the entire range of temperatures found in conventional steam generating equipment, which generally lie between degrees F. Furthermore, these compounds are believed to be effective even at temperatures below degrees F. The amount of neutralized erythorbate required to effectively scavenge oxygen from the water of a steam generating system is dependent upon the amount of oxygen actually present therein, as well as upon the pH of the system and other system characteristics. Therefore, the optimal concentration of the present scavenging agents will have to be determined on a case by case basis. In general, however, it is believed that feedwater concentrations of at least 0. A desirable ammonium neutralized erythorbate concentrate can be made by preparing a 25 percent by weight erythorbic acid solution and adding sufficient ammonium hydroxide to adjust the pH of the solution to at least about 5. Adjustment to pH 6. This 25 percent ammonium neutralized erythorbate concentrate has been found to have excellent activity retention both at

room temperature and at degrees F. The degrees F. Although the present scavenging agents may be added to the steam generating equipment at any convenient point, it is more efficient to treat the boiler feedwater, preferably as it comes from the degasifier. Residence times prior to steam formation should be maximized to obtain maximum corrosion protection. While the treatment chemical will control corrosion even when residence times are as low as minutes, residence times of minutes or more are preferred, if they can be achieved in the particular steam generating equipment being treated. The scavenging agents employed in the practice of the present invention have been found to be not only good oxygen scavengers, but also excellent passivating agents for steel, steel alloys and other metallic surfaces. These compounds outperform both hydrazine and sulfite in passivation. They preferentially interact with metal surfaces enhancing passive films formation in mild steel and copper alloy surfaces. As in the case of oxygen scavenging to control corrosion, the optimal treatment levels for passivation must be determined on a case by case basis. However, in most systems, satisfactory passivation can be achieved during the initial hours of operation of the system with the present treatment by maintaining the dosage chosen for oxygen scavenging. Finally, while the present scavenging agents may be used alone in the practice of the present invention, their activity may be enhanced by the addition of pro-oxidant catalysts such as copper, nickel and iron. The catalyst level in the feedwater typically should be at least about 5 ppb by weight. The following examples are intended to illustrate the practice of the present invention. The utility steam generating system handled a variable load ranging from , lb. The boiler had no deaerator. Its preboiler system consisted of a series of six stage heaters and an economizer. The treatment program already in place at the time of the present testing entailed: The control limits for the system were as follows: The ammonium hydroxide neutralized erythorbic acid was initially fed at the same locations as the hydrazine. The first and lowest dosage was 0. The existing treatment program at this steam generating plant utilized a 0. The ammonia neutralized erythorbic acid treatment significantly outperformed hydrazine in oxygen removal when fed at equivalent concentrations. In fact, where hydrazine was unable to meet the specified 5 ppb oxygen control limit, the ammonium neutralized erythorbate did. Furthermore, iron levels at the condensate hotwell and feedwater pump sample points were significantly lower than experienced with hydrazine, thus indicating that the ammonia neutralized erythorbic acid treatment produced enhanced corrosion inhibition in this system. Finally, conductivity and pH in the boiler water remained consistent, indicating that the ammonia neutralized erythorbic acid treatment had little effect on the phosphate program already in place. EXAMPLE 2 In this example, metal surface passivation was examined in an experimental boiler utilizing a shell and tube heat exchanger to simulate a stage heater. Feedwater in this experimental system was made up with an oxygen content of 80 ppb. The inlet temperature to the heat exchanger was degrees F. Feedwater treated with hydrazine was compared with feedwater treated with a 25 percent by weight erythorbic acid solution neutralized to pH 6. Metallographic examination of the tube surfaces showed a uniform adherent magnetite film with the erythorbic acid treatment that was clearly superior to that formed with hydrazine. The erythorbic acid treated tubes were free of pitting and better than those treated with hydrazine, which, in turn, were better than those contacting untreated feedwater. It was found that, at room temperature, sodium erythorbate and ammonium neutralized erythorbate react with oxygen at approximately equal rates. At high temperatures e. While the present invention is described above in connection with preferred or illustrative embodiments, the embodiments are not intended to be exhaustive or limiting of the invention. Rather, the invention is intended to cover any alternatives, modifications, or equivalents that may be included within its spirit and scope, as defined by the appended claims. A method of removing dissolved oxygen from boiler feedwater and passivating boiler metal surfaces comprising adding to said boiler feedwater an oxygen scavenging amount of an ammonium or amine neutralized erythorbate at a pH of at least about 5. The method of claim 1 wherein ammonium neutralized erythorbate is used. The method of claim 2 wherein said ammonium neutralized erythorbic acid is added to said feedwater at a level of at least 0. The method of claim 2 wherein said ammonium neutralized erythorbate solution is pH adjusted to about 6. The method of claim 2 wherein a pro-oxidant catalyst is utilized. The method of claim 2 wherein said catalyst is utilized at a level of at least about 5 ppb by weight. The method of claim 2 wherein said catalyst is chosen from the group comprising copper, nickel and iron. The method of claim 2 wherein said pH is at least about

pH 6.

**Chapter 3 : Scavenging (automotive) - Wikipedia**

*The present invention is directed to methods of reducing the amount of hydrogen sulfide in hydrogen sulfide-containing aqueous or wet gaseous mediums without solids formation.*

This invention comprises adding an effective amount for the purpose of glyoxal or glyoxal in combination with formaldehyde or glutaraldehyde to the desired hydrogen sulfide-containing medium. The reactivity between various aldehydes and sulfidic compounds H<sub>2</sub>S, mercaptans, etc. For example, Marks in U. Consumption of the hydrogen sulfide liberated by acidification of sulfide-containing deposits increased the safety of such operations. Decreased corrosivity of the aldehyde-containing acids is also disclosed in the prior art, sometimes with the addition of ancillary corrosion inhibitors. STR1 Two such sulfide-active compounds disclosed by Roehm are acrolein and 3-butenone. Formaldehyde, formaldehyde with SO<sub>3</sub><sup>-2</sup>, and acrolein are all commercially used hydrogen sulfide H<sub>2</sub>S scavengers. However, formaldehyde produces a solid reaction product and reverts readily to formaldehyde and free H<sub>2</sub>S. Acrolein is more expensive than formaldehyde as well as extremely toxic and dangerous to handle. The use of SO<sub>3</sub><sup>-2</sup> with formaldehyde eliminates the re-release of H<sub>2</sub>S but not solids formation. Despite the prior art approaches to H<sub>2</sub>S scavenging, the provision of a single compound or group of compounds capable of providing the H<sub>2</sub>S scavenging function while not producing a solid reaction product and without stringent handling problems is highly desirable from a commercial point of view. Such a compound or compounds would provide suitable H<sub>2</sub>S scavengers for systems where solids must be avoided. These needs are effectively met by utilization of the hydrogen sulfide scavenging methods of the present invention. Glyoxal corresponds to the chemical formula STR2 Additionally, it has been found that glyoxal functions as an effective H<sub>2</sub>S scavenger without producing a solid reaction product when the glyoxal is used in combination with formaldehyde or glutaraldehyde in an effective amount for the purpose. This is surprising since glyoxal is a di-functional analog of formaldehyde and would therefore be expected to form solid polymeric products. Furthermore, glyoxal is not a "sulfide active" carboxyl compound as defined by Roehm in U. Unexpectedly, the use of glyoxal produces a soluble and relatively stable reaction product. Glyoxal approaches the H<sub>2</sub>S scavenging rate of acrolein without the constraining handling problems presented by the use of acrolein. Moreover, unlike the present invention, the use of SO<sub>3</sub><sup>-2</sup> with formaldehyde eliminates re-release of H<sub>2</sub>S but does not inhibit solids formation. The glyoxal and its combination with formaldehyde or glutaraldehyde may be added to any aqueous medium containing hydrogen sulfide for which the amount of hydrogen sulfide is desired to be reduced without solids formation. It is believed that glyoxal and its mixtures may be effective for use in wet gaseous mediums containing hydrogen sulfide to reduce the amount of hydrogen sulfide without the formation of a solid reaction product by contacting the wet gaseous medium with an effective amount for the purpose of a glyoxal or its aforesaid mixtures. Wet gaseous mediums are those containing H<sub>2</sub>O in any concentration. Preferably, the aqueous or wet gaseous medium has a pH from neutral to alkaline. Glyoxal and its mixtures are suitable H<sub>2</sub>S scavengers for use in controlling sour leaks into cooling water systems, oil and gas production systems, and other similar systems. The amount of glyoxal and mixtures thereof used in accordance with the present invention depend on the severity of the H<sub>2</sub>S problem in the medium being treated. Glyoxal-rich mixtures are desired to achieve effective H<sub>2</sub>S rapid scavenging. It is thought that the preferred amount of glyoxal to be added to the medium being treated is that amount required to provide a glyoxal: H<sub>2</sub>S molar ratio from about 1: Most preferably, the glyoxal: H<sub>2</sub>S molar ratio is about 2. H<sub>2</sub>S molar ratio from about 0. H<sub>2</sub>S molar ratio of about 3: The invention will be further illustrated by the following examples which are included as being illustrations of the invention and which should not be construed as limiting the scope thereof. A four-neck lid allowed introduction of a glass pH electrode, a specific ion electrode and a double-junction reference electrode for each. Both the pH and the mV response of the specific ion electrode were recorded continuously throughout each test run on a chart recorder. Standard conditions for all test runs were: The brine was purged with O<sub>2</sub>-free N<sub>2</sub> for at least two hours before sulfide addition. Sulfide addition to the brine was made in two increments. The first addition was about 10 ppm and the second was about 90 ppm, for a total of about ppm.

The mV and pH readings were noted for each addition after suitable equilibration. All mV readings were corrected for slight pH variations which occurred during the test runs. The test runs were allowed to equilibrate overnight after treatment addition. However, for the results reported in Table IV, the exact solution volume of each test run was used to calculate the treatment concentration and more accurate ratios are reported in Table IV. The results obtained for glyoxal, acrolein, formaldehyde and glutaraldehyde with each tested separately are reported in Table I. Treatment Molar Ratio Time mins. However, these results also show that glyoxal is a very rapid H<sub>2</sub>S scavenger and eventually attains about the same effectiveness of acrolein. The results in Table I further indicate that formaldehyde and glutaraldehyde are considerably less effective H<sub>2</sub>S scavengers. Glyoxal, acrolein and glutaraldehyde were not observed to form solid reaction products. Solids were observed to precipitate after four hours when formaldehyde was used. Glyoxal, acrolein, formaldehyde and glutaraldehyde were also tested as H<sub>2</sub>S scavengers in the presence of SO<sub>3</sub><sup>-2</sup> and the results are reported in Table II with each tested separately. Treatment Molar Ratio mins. Solids were observed in the formaldehyde test run after four hours. Solids were not produced for these three aldehydes during the test runs. A comparison of the H<sub>2</sub>S scavenging performance of glyoxal, glyoxal in combination with formaldehyde, and glyoxal in combination with glutaraldehyde was conducted and the results are reported in Table III. For each test run in Table III, the total aldehyde: H<sub>2</sub>S molar ratio used was about 2. Additional test runs were conducted to better characterize the H<sub>2</sub> reactivity of glyoxal and its mixtures and the results are reported in Table IV. Field tests were also conducted at an oil production test well and a gas production system for an evaluation of glyoxal as an H<sub>2</sub>S scavenger. The results from these field tests showed rapid and significant initial reductions in H<sub>2</sub>S concentration for the natural gas, crude oil, and produced water phases. However, a gradual liberation of H<sub>2</sub>S from the glyoxal treated waters occurred. But at both the oil production test well and the gas production system, the water pH was acidic and in the 4. But at a pH of about 9, the predominant sulfide species is the non-volatile HS<sup>-</sup> ions. Thus, it is thought that higher temperature, low pH or gas sparging increase the volatility of H<sub>2</sub>S from solution. This, in turn, results in decomposition of the reaction product to glyoxal and H<sub>2</sub>S or HS<sup>-</sup> in order to maintain equilibrium. Claims 15 I claim: A method for reducing the amount of hydrogen sulfide in a hydrogen sulfide-containing aqueous medium without solids formation, wherein said aqueous medium has a pH from neutral to alkaline, which method comprises adding to the aqueous medium an effective amount for the purpose of a glyoxal. A method according to claim 1, wherein said glyoxal is added in an amount to provide a glyoxal: A method according to claim 1, wherein said aqueous medium has a pH of about 9. A method according to claim 1, wherein the addition is conducted at ambient temperature. A method according to claim 6, wherein said aqueous medium has a pH of about 9. A method according to claim 6 wherein the addition is conducted at ambient temperature. A method according to claim 10, wherein said aqueous medium has a pH of about 9. A method according to claim 10, wherein the addition is conducted at ambient temperature. A method for reducing the amount of hydrogen sulfide in a hydrogen sulfide-containing wet gaseous aqueous medium without the formation of a solid reaction product, wherein said aqueous medium has a pH from neutral to alkaline, which method comprises contacting said wet gaseous medium with an effective amount for the purpose of a glyoxal. A method according to claim 13, wherein said glyoxal is added in amount to provide a glyoxal: A method according to claim 13, wherein said contacting is conducted at ambient temperature.

**Chapter 4 : What is scavenging and why is it important in ship engines?**

*Scavenging methods There are different types of scavenging methods that are used in both two and four stroke engines but the basic principle remains the same, i.e. the fresh air enters the cylinder by the opening of the port during the downward stroke of the piston and continues till the port is closed by the upward stroke of the piston.*

In the method, an aldehyde-releasing compound, which is high temperature stable and is highly water-soluble, is introduced to a hydrocarbon fluid stream as a scavenger for sulfhydryl compounds. The aldehyde-releasing compound is allowed to mix with the hydrocarbon fluid stream and the aldehyde-releasing compound is allowed to react with the sulfhydryl compounds present in the hydrocarbon fluid stream, thereby reducing the presence sulfhydryl compound in the hydrocarbon fluid stream. Generally, these hydrocarbon fluids are mixed with other impurities that are undesirable. One of these impurities is sulfides, in particular, sulfhydryl compounds including, but not limited to hydrogen sulfide H<sub>2</sub>S. The presence of hydrogen sulfide and other sulfhydryl compounds is objectionable because these compounds may react the hydrocarbon fluid, are often corrosive, flammable, poisonous and emit a noxious odor. The presence of hydrogen sulfide poses significant environmental and safety concerns to personnel and operations, and can make the hydrocarbon fluid unacceptable for commercial purposes This is due in part to the fact that hydrogen sulfide is highly flammable, highly toxic when inhaled 8 h of exposure at ppm has been reported to cause death while levels of 1 , ppm can cause death within minutes , highly corrosive, and malodorous. Further, corrosion and scale deposits resulting from the presence of hydrogen sulfide in contact with metallic surfaces, such as carbon steel pipes can further disrupt industrial operations via the plugging of pipes, valves, nozzles, and the like. The latter is an important consideration due to sulfide poisoning of cracking catalysts. Further, in both the refining industry and geothermal power industry, cooling tower process water can contain moderate to high levels of hydrogen sulfide, both causing significant solids development, as well as increasing the level of oxidant demand so as to make oxidants unviable options for microbial control in these systems. These processes are often call "sweetening" of the hydrocarbon fluid. Components added to hydrocarbon fluids to reduce or eliminate hydrogen sulfide or sulfhydryl compounds are commonly called a "scavenging agent" or a "scavenger". Common techniques utilize either absorption with a solvent or solid phase material with subsequent regeneration of the absorbent, or reaction with a suitable substance or substrate "scavenger" that produces a corresponding reaction product. The reaction has often involved the reaction of hydrogen sulfides with various types of aldehydes. Other examples include U. Nonetheless, both acrolein and 3-butenone are hazardous, highly toxic chemicals limiting extensive use in a wider variety of applications. The mixture improves the overall scavenging capacity of triazines, but whether complete removal is achieved for a theoretically stoichiometric amount is not reported. However, it is known that typically triazines, such as hydroxyethyl triazines, do not scavenge H<sub>2</sub>S stoichiometrically i. These drawbacks include, for example, the formation of compounds that participate in aqueous environments, such as trithianes that are produced when sulfhydryl compounds are reacted with formaldehyde. In the case of triazines that release formaldehyde, these compounds also release alkyl amines which can raise the pH in the system, potentially leading to scale deposition. In addition, triazine compounds, such as the commonly used 1 ,3,5-tris 2- hydroxyethyl - hexahydro-s-triazine, is considered to be highly toxic and corrosive. As such, this compound has many drawbacks. Hence, in order to prevent problems associated with hydrogen sulfide and other sulfhydryl compounds in the production system and to improve the quality of the oil and gas produced, it is desirable to be able to use the chemical as early as possible in the production process, such as via downhole injection. Ideally, the scavenge for hydrogen sulfide should be non-hazardous, non-corrosive, biodegradable, and have a scavenging performance over a wide temperature range and pH range. The present invention provides an answer to that need. In this method a high temperature stable, highly water-soluble aldehyde-releasing compound is first provided. In this method, the production well or injection well has a downhole additive addition means. This downhole is accessible from the surface via known means. The aldehyde-releasing compound is added to a production well via the downhole additive addition means during production of oil or

gas from the production well. It has also been surprisingly discovered that these compound do not exhibit the drawbacks of the compounds which have been suggested to be used as sulfhydryl compound scavengers. Suitable aldehyde-releasing compounds include hydantoins, imidazolidinyl ureas, dimethyloxazolidines, and glutaraldehydes. Of these compounds, hydantoins are of the most interest. Hydantoins are known in the art to be high temperature stable, safe to the environment and have been used in treating bodies of water for microbial control. As such, hydantoins are considered to be a safe alternative to other scavengers which may be toxic to the environment and those operating the production facility. Exemplary hydroxyalkylhydantoins useable as the aldehyde-releasing compound include, but are not limited to, 1-hydroxymethyl-5,5-dimethyl-hydantoin also known as monomethyloldimethylhydantoin MDMH, 3-hydroxymethyl-5,5-dimethylhydantoin. Exemplary bis hydroxyalkyl hydantoins useable as the aldehyde-releasing compound include, but are not limited to, 1,3-bis hydroxymethyl -5,5- dimethylhydantoin as known as dimethyloldimethylhydantoin DMDMH. Exemplary dialkylhydantoins useable as the aldehyde-releasing compound include, but are not limited to, 5,5-dimethylhydantoin. In addition, mixtures of the hydantoins may also be used. The mixture of hydantoins described in U. Patent 5,, have a low free formaldehyde concentration, which helps avoid the problems mentions above regarding the use of formaldehyde. Alternatively, solid hydantoins may also be used and the solid hydantoins described in U. The disclosure of each of U. Any known method of introducing the aldehyde-releasing compound into the hydrocarbon fluid stream may be used. The aldehyde-releasing compound may be a liquid composition, or a solid. It also may be part of larger composition or mixed with other ingredients used to treat the hydrocarbon fluid. For example, the aldehyde releasing composition may be part of treatment package that is added to the hydrocarbon. Other ingredients which may be part of the treatment package include, for example, corrosion inhibitors, scale inhibitors, paraffin inhibitors, hydrate inhibitors and the like. In gas production wells, the aldehyde-releasing compound should be compatible with deliquification additives and antifoamers which may be part of the additive package. The aldehyde-releasing compound should be compatible the other additives and should be non-reactive with the other additives. Aldehyde releasing compounds, such as triazine aldehyde releasing compound which have precipitates as a by-product are not intended to be included in the aldehyde-releasing compounds of the present invention. Typically, hydrocarbon fluid production wells have production piping. This production piping is generally provided with a downhole additive means that allow additives to be added to the hydrocarbon fluid being produced from the production well. Downhole additive means includes, for example a capillary string, umbilical cord, a perforation in the annulus of a production pipe, addition at the backside of the production or injection well or other similar means that can effectively add an additive to the hydrocarbon fluid. Likewise, the additive may be added to an injection well in the injection fluid, or may be added at another location in the production piping. An injection well is a well that produces the hydrocarbon fluid by injecting a fluid into the well, thereby causing the hydrocarbon fluid to be expelled with the fluid being injected into the well. In one embodiment, the injection well is injected with brine and the aldehyde releasing compound is added to the brine injected into the well. In any event, in this embodiment, the aldehyde-releasing compound is placed in the hydrocarbon fluid stream of the well below the ground. By adding the aldehyde-releasing compound, the aldehyde releasing compounds are given a period of time to react with and scavenge the sulfhydryl compound from the hydrocarbon fluid. Continuous addition is generally more advantages since it promotes a continuous flow of the aldehyde-releasing compound into the hydrocarbon fluid, which allows for effective continuous control of the sulfhydryl compounds in the hydrocarbon fluid. In addition, the aldehyde-releasing compound may be added in a continuous fashion with periodic boost or batch increase to counter act an increase in the presence of the sulfhydryl compound in the hydrocarbon fluid. For example, the aldehyde-releasing compound may be added to the hydrocarbon fluid at the gas lift or the pump in the production system. Examples of surfactants include, but are not limited to, quaternary ammonium compounds, polymers and co-polymers of ethylene oxide and propylene oxide, ethoxylated and propoxylated esters of fatty acids, fatty alkyl amine oxides, fatty acid imidazolines and betaines, and nonylphenol ethoxylates. The alkyl groups are any linear, branched or cyclic saturated hydrocarbyl groups having the stated number of carbon atoms. Arylalkyl groups are alkyl groups substituted

with an aryl group, preferably with a phenyl group, such as benzyl phenylmethyl or phenylethyl. The halides are generally fluorides, chlorides, bromides or iodides, preferably chlorides or bromides. C mono- or dicarboxylates are anions derived from saturated or unsaturated mono- or dicarboxylic acids having 2 to 20 carbon atoms, such as acetate, propionate, butyrate, pentanoate, hexanoate, octanoate, decanoate, dodecanoate laurate, tetradecanoate myristate, hexadecanoate palmitate, octadecanoate stearate, oleate, linolate, oxalate, malonate, succinate, glutarate, adipate, 1,8-octanedioate, 1,10-decanedioate, 1,12-dodecanedioate and the like. Borates may be monoborates containing the  $\text{BO}_3^-$  anion or polyborates such as di-, tri-, tetra-, penta-, hexa-, or octaborates. Sulfonates may be alkanesulfonates, such as methanesulfonate or trifluoromethanesulfonate, or arenesulfonates, such as benzene- or toluenesulfonate. Sulfates may be "neutral" sulfates or "acid" sulfates hydrogensulfates, bisulfates. The upper limit of the aldehyde-releasing compound is unlimited. Generally, more of the aldehyde-releasing compound added, the faster the sulfhydryl compound will be scavenged. The upper limit is essentially limited to the cost of the aldehyde-releasing compound to the benefit obtained. Typically, the aldehyde-releasing compound or mixtures of compounds will be added to the hydrocarbon in an amount between about 1 to about 10 moles of the aldehyde releasing compound or mixture per mole of the sulfhydryl compound present in the hydrocarbon fluid. Generally, there will be between about 2 and about 5 moles of the aldehyde releasing compound or mixture of compounds per mole of the sulfhydryl compound present in the hydrocarbon fluid. Water is often generated as an impurity of hydrocarbon production wells and water can be used as the injection fluid in injection wells. Since sulfhydryl compounds, particularly hydrogen sulfide are water soluble, the water generated by the well can contain amounts of the sulfhydryl compound, which can transfer to the hydrocarbon fluids generated by the well, thereby souring the hydrocarbon gas and liquid. The average hydrogen sulfide content is approximately ppm. Hydrogen sulfide in the gas was measured upstream of the separator unit, while the scavenger was injected downhole through the annulus of the downpipe and into the well. As shown in Table 1, the efficiency of the composition of the present invention is described. The average hydrogen sulfide content is approximately ppm for the three streams. The composition was injected in the hydrocarbon fluid stream through an injection nozzle located below the ground surface. Hydrogen sulfide in the gas was measured approximately 4, m 5, yards from the injection point. The scavenging efficiency of the product is exemplified in Table 2. The average hydrogen sulfide content is approximately 36 ppm, prior to treatment. Hydrogen sulfide in the gas was measured approximately 1, m 1, yards from the injection point. Table 3 shows the efficiency of the scavenger of the present invention. Accordingly, it is intended to embrace all such changes, modifications, and variations that fall within the spirit and broad scope of the appended claims. Claims What is claimed is: A method for reducing sulfhydryl compounds from a hydrocarbon fluid stream, said method comprising i providing a high temperature stable, highly water soluble aldehyde-releasing compound selected from the group consisting of hydantoins, imidazolidinyl ureas, dimethylloxazolidines, glutaraldehydes, and mixtures thereof; ii adding an effective amount of the aldehyde-releasing compound to a hydrocarbon fluid stream containing a sulfhydryl containing compound; and iii allowing the aldehyde-releasing compound to mix into the hydrocarbon fluid stream and react with at least a portion of the sulfhydryl compound. The method according to claim 1, wherein the aldehyde-releasing compound is a compound. The method according to claim 1, wherein the aldehyde-releasing compound comprises a hydantoin. The method according to claim 2, wherein the hydantoin comprises a hydroxymethyl hydantoin, a bis hydroxymethyl hydantoin or a mixture thereof. The method according to claim 4, wherein the hydroxymethylhydantoin is selected from the group consisting of 1-hydroxymethyl-5,5-dimethylhydantoin, and 3-hydroxymethyl-5,5-dimethylhydantoin, and the bis hydroxymethyl hydantoin is 1,3-bis hydroxymethyl-5,5-dimethylhydantoin. The method according to claim 1, wherein the sulfhydryl compound present in the hydrocarbon fluid comprises hydrogen sulfide. The method according to claim 1, wherein the aldehyde-releasing compound is continuously fed to the hydrocarbon fluid. The method according to claim 1, wherein the aldehyde-releasing compound is fed to hydrocarbon fluid in a batchwise manner. The method according to claim 1, wherein the aldehyde-releasing compound is added in amount of at least 0. The method according to claim 9, wherein the aldehyde-releasing compound is added in amount between about 1 to about 10 moles of the aldehyde-releasing compound per mole of the sulfhydryl

present in the hydrocarbon fluid stream to be treated. A method for reducing sulfhydryl compounds from an oil and gas production well or injection well, said method comprising i providing a high temperature stable, highly water soluble aldehyde-releasing compound, selected from the group consisting of hydantoins, imidazolidinyl ureas, dimethyloxazolidines, glutaraldehydes, and mixtures thereof ; and ii adding an effective amount of the aldehyde-releasing compound to a well having a downhole additive means, the aldehyde-releasing compound being added via the downhole additive means during production of oil or gas from the production well or injection well. The method according to claim 1 1 , wherein the aldehyde-releasing compound is added to a hydrocarbon fluid containing the being produced from the production well or the injection well.

*A method of reducing the amount of sulfhydryl compounds from sour hydrocarbon fluids is described. In the method, an aldehyde-releasing compound, which is high temperature stable and is highly water-soluble, is introduced to a hydrocarbon fluid stream as a scavenger for sulfhydryl compounds.*

Red fruits, as rich antioxidant foods, have gained over recent years capital importance for consumers and manufacturers. The industrial extraction of the phenolic molecules from this source has been taking place with the conventional solvent extraction method. New non-conventional extraction methods have been devised as environmentally friendly alternatives to the former method, such as ultrasound, microwave, and pressure assisted extractions. The aim of this review is to compile the results of recent studies using different extraction methodologies, identify the red fruits with higher antioxidant activity, and give a global overview of the research trends regarding this topic. As the amount of data available is overwhelming, only results referring to berries are included, leaving aside other plant parts such as roots, stems, or even buds and flowers. Several researchers have drawn attention to the efficacy of non-conventional extraction methods, accomplishing similar or even better results using these new techniques. Some pilot-scale trials have been performed, corroborating the applicability of green alternative methods to the industrial scale. Blueberries *Vaccinium corymbosum* L. However, several new up and coming berries are gaining attention due to global availability and elevated anthocyanin content. Introduction In developed countries, alimentation is more focused on complimentary aspects than merely covering major component needs. Because of this, the so called red fruits, or berries, have recently attracted a lot of attention for their antioxidant properties, which are related to the high concentration of polyphenols present in them. In addition, their consumption worldwide has notoriously increased, and red fruits are nowadays not only consumed fresh but also used in cosmetics and dietary supplements. To benefit from these molecules in nutraceuticals, creams and functional foods, an extraction needs to be performed in order to obtain an antioxidant-rich concentrate from a variety of edible berries. The habitual aim is to obtain the maximum extraction yield of the compounds of interest, those that have more antioxidant activity, and, therefore, are capable of being more beneficial to human health, as well as being substitutes for synthetic preservatives, the latter having gained bad press over recent years, especially when part of the final product. In the last few years, several studies analyzing the composition and the antioxidant properties of typical red fruits have been published frequently, and wide research has been taking place all over the world to find the optimal extraction methods to obtain richly antioxidant products for a range of berries. Although conventional solvent extraction is the most widespread technique for the extraction of antioxidant compounds from red fruits, new non-conventional methods have surfaced as environmentally friendly alternatives to the former method, such as ultrasound [ 1 ], microwave [ 2 ], and pressure assisted extractions [ 3 ], applied alone or together with solvent use, to reduce the energy and solvent requirement. Although extraction techniques seem to have received much attention from researchers, the effects of cultivar [ 4 ], storage [ 5 , 6 ], and drying techniques [ 7 , 8 ] have also been studied. This review gathers some of the latest results published in scientific journals about antioxidant extraction and activity of red fruits, in order to facilitate a wider vision of this topic. Phenolic Acids and Anthocyanidins in Red Fruits Berries are characterized by the high amount of antioxidant molecules. These chemical compounds are a group of secondary metabolites that prevent the fruit from oxidation due to environmental factors, such as light, air, oxygen, and microbiological attacks. Phenolic antioxidants interfere with the oxidation process as free radical terminators and sometimes also as metal chelators. Phenolic compounds or polyphenols are a group of hydroxylated molecules very susceptible to oxidation. Several studies have found them to have various biological properties, such as anti-proliferative, anti-diabetic, anticancer, anti-microbial, anti-inflammatory, antiviral, and especially important for this review: They have different structures but in general contain an aromatic ring with one or more hydroxyl groups. The radical scavenging capacity of phenolic antioxidant molecules is based on the ability to become radicals that are more stable compared to the majority of free radical species, due to the stabilization of the free electron by delocalization on the aromatic ring of the

phenolic compounds. A classification of phenolic antioxidants can be made, the most important being phenolic acids and anthocyanidins, as a subgroup of flavonoids. Phenolic acids can be divided into two categories: The first group includes molecules such as hydroxybenzoic, gallic, vanillic, and ellagic acid Figure 2 a. In the second group p-coumaric, caffeic, ferulic, chlorogenic Figure 2 b , and hydroxycinnamic acid can be found. These compounds can be widely found in berries, and each type of berry contains a characteristic profile of phenolic molecules. Anthocyanins are water-soluble plant pigments responsible for the blue, purple, and red color of many plant tissues [ 10 ]. Anthocyanidins are based on the flavylium ion, or 2-phenylchromenylium. The variety of chemical groups that can substitute the different positions R1, R2 create the anthocyanidins found in nature. A simplification of this ion, focusing on the common structures in red fruits can be seen in Figure 3. There are about 17 anthocyanidins found in nature, whereas only six of them, cyanidin, delphinidin, petunidin, peonidin, pelargonidin, and malvidin, are present in most foods [ 11 ]. When anthocyanidins are coupled to sugars, anthocyanins are formed. In red fruits, anthocyanins are mostly 3-glucosides of the anthocyanidins, cyanidinglucoside being the most common compound in the majority of berries Figure 4. Among flavonoids, anthocyanins are antioxidants that play an important role in reducing the risks of various human degenerative diseases [ 3 ]. In general, the stability of anthocyanidins is pH-dependent. At acidic or basic pH the highly conjugated phenolic groups of the anthocyanidins protonate and deprotonate causing a change in electronic distribution which, at the same time, affect the absorption wavelength and the perceived color.

**Berries and Red Fruits:** The most well-known red fruits are strawberry, raspberry, blueberry, blackberry, and cranberry, which are also the ones with the most accessible information about them. Chokecherries, elderberries, mulberries, and other less frequent fruits are also commonly considered as red fruits. Berries, in general, are rich in sugars glucose, fructose , but low in calories. They contain only small amounts of fat, but a high content of dietary fiber cellulose, hemicellulose, pectin ; organic acids, such as citric acid, malic acid, tartaric, oxalic, and fumaric acid; and certain minerals in trace amounts [ 12 ]. In Table 1 there is a summary of the nutritional values for the most well-known red fruits. In this section only the most typical berries will be commented upon. Later on in this review, several research papers will be referenced which not only use common but also novel red fruits for antioxidant extraction, due to the continuous appearance of berries from different parts of the world with interesting properties. *Fragaria* is a genus of flowering plant in the rose family, Rosaceae, commonly known as strawberry for their edible fruits. There are more than 20 described species and many hybrids and cultivars. In a study conducted on strawberries using liquid chromatography for the identification of antioxidant compounds, four anthocyanins were readily found: Identity of the first two anthocyanins was confirmed by spiking with authentic standards whereas pelargonidinrutinoside was tentatively assigned by comparison of the peak online spectrum with a spectrum presented by another author. Strawberries are an excellent source of potassium, fiber, many B vitamins, vitamin C, vitamin K, manganese, iodine, folate, omega-3 fatty acids, magnesium, and copper [ 15 ]. *Rubus idaeus* *Rubus idaeus* raspberry, also called red raspberry or occasionally as European raspberry to distinguish it from other raspberries is a red-fruited species of *Rubus* native to Europe and northern Asia and commonly cultivated in other temperate regions. Raspberries have very interesting nutritional properties due to their high amount of fiber and antioxidant compounds, including phenolic acids, flavonoids, and lignans with a reduced calorie input. The presence of ellagitannins and anthocyanidins not only contribute to the healthy attributes but also to their attractive color [ 16 ]. Quercetin is the most representative flavonol in red raspberries [ 17 ]. *Rubus fruticosus* Blackberry not to be confused with black raspberry is a bushy plant in the rose family, native to Europe, Asia, and North Africa. It was found that cyanidinglucoside representing This result is in agreement with data reported by other authors [ 11 ]. *Vaccinium corymbosum* *Vaccinium corymbosum*, the northern highbush blueberry, is a North American species of blueberry which has become a food crop of significant economic importance. Recent studies proving the effectiveness of blueberries as a good source of antioxidants, necessary for a balanced diet and the added anticancer properties have resulted in this fruit achieving more popularity around the world. The increasing demand is being covered with higher production, especially from the American continent, which delivers more than three quarters of the global production of this fruit. *Vaccinium myrtillus* Three times smaller than the blueberry *Vaccinium corymbosum* , but similar in

appearance and flavor, *Vaccinium myrtillus* is also known as the European blueberry, or bilberry. Several clinical trials demonstrated the benefits of *Vaccinium myrtillus*-extracted anthocyanosides in the management of visual disorders in humans [ 20 ]. The main anthocyanins found in bilberry extract are cyanidinglucoside. Common cranberry *Vaccinium oxycoccos* and the similar looking small cranberry *Oxycoccos microcarpus* are evergreen dwarf shrubs with small, narrow leaves and red edible fruit. American cranberry *Vaccinium macrocarpon* is a major commercial crop in eastern Canada and north-eastern USA [ 21 ]. Quercetin is one of the major significant flavonoids occurring in cranberries. While the previously described berries are widely known, there are many others which have been studied for their antioxidant capacity, whether they can be found worldwide or only grow in restricted areas, which are mainly studied or consumed by the local population. Most Common Antioxidant Content Determination and Radical Scavenging Assays in Red Fruits In this section the key information about antioxidant content is highlighted, and the most commonly used assays to determine the quantity of these molecules and their antioxidant power are explained. The chemical reaction is based on the electron transfer from phenolic compounds and the measurement of the absorbance of the blue colored complexes at nm. Gallic acid is used as a standard, and results are usually expressed as mass of Gallic Acid Equivalents GAE per gram of mass of the sample or extract. One of the main disadvantages is that the TPC method is not specific, as the reagent can be reduced by other compounds other than phenolics [ 23 ]. The high values obtained for TPC could result from interference of other reducing substances, such as ascorbic acid or reducing sugars [ 22 ]. Anthocyanin pigments undergo reversible structural transformations with a change in pH manifested by different absorbance spectra. The oxonium form predominates at pH 1. The pH-differential method is based on this reaction and allows accurate and rapid measurements of the total amount of anthocyanins, even in the presence of polymerized degraded pigment and other interfering compounds [ 24 ]. Cyanidinglucoside is used as a standard, and results are usually expressed as mass of cyanidinglucoside C3G per gram of mass of the sample or extract. Ascorbic Acid Content Also known as vitamin C, ascorbic acid and its derivatives are known to have antioxidant properties, acting both directly, by reaction with aqueous peroxy radicals, and indirectly, by restoring the antioxidant properties of fat-soluble vitamin E [ 25 ]. Regarding red fruits, however, it has been found that polyphenols and anthocyanins contribute substantially to the antioxidant intake [ 26 ], while ascorbic acid only makes a minor contribution to the total antioxidant capacity [ 27 ]. Ascorbic acid content can be determined by a variety of methods, including titration, spectrophotometry, chromatography or voltammetry [ 28 ]. Radical Scavenging Assays Antioxidant capacity assays can be divided into two categories according to their reaction mechanisms: The first one, mainly found in non-ionizing solvents, consists in the transfer of a hydrogen atom from the substance that acts as the antioxidant to the free-radical. The HAT-based methods are generally composed of a synthetic free radical generator, an oxidizable molecular probe, and an antioxidant [ 30 ]. The second category, Single Electron Transfer SET , detects the ability of a potential antioxidant to transfer one electron to reduce any compound, including metals, carbonyls, and radicals. It involves one redox reaction with the oxidant also as a probe for monitoring the reaction as an indicator of the reaction endpoint. SET and HAT reactions may occur together and the mechanism finally dominating in a system is determined by the antioxidant characteristics. DPPH 2,2-diphenylpicrylhydrazyl radical assay can be included in both categories. Each radical scavenging assay relies on a colorimetric or fluorescent change due to the scavenging of the radicals added to the solution. In ORAC, antioxidant compounds in the sample inhibit fluorescence decay caused by the reaction of fluorescein with peroxy radicals. In this last case, the lower the IC<sub>50</sub> value, the higher the antioxidant capacity obtained. Trolox is a water soluble vitamin E analogue used as a standard scavenger. The chemical reactions between the antioxidant sample and the reagent that take place in radical scavenging assays are summarized in Figure 5 , and an overview of each assay can be seen in Table 2. An important factor to take into account is the concentration of the extract with which the scavenging assay is made. Extracts with higher concentration lead to better results, higher antioxidant capacity samples. To undertake a correct comparison, this concentration should be taken into consideration when looking at different data. Common Methods for the Extraction of Antioxidants from Red Fruits The characteristics of the extract obtained from red fruits are determined by two main factors: The first one determines the amount of antioxidants in the

berries, while the second governs the ability to extract those molecules from the vegetable matrix.

**Chapter 6 : Scavenging in Two-Stroke Engines**

*In this study, three radical scavenging methods were used to assess the determination of potential radical scavenging activities of tannic acid, namely ABTS + radical scavenging, DPPH radical scavenging and  $\dot{A}$ -superoxide anion radical scavenging activity.*

The present invention generally relates to a method for manufacturing a dye scavenging substrate. Although fading of dyes is more prevalent from new, unlaundered, or heretofore infrequently laundered goods, even articles with considerable fastness to washing, or having a long history of numerous previous launderings, may continue to bleed small amounts of dyestuff or colorant into the bath or wash water. The well known, but aggravating and undesirable result of such fading is that at least part of the extraneous, free flowing dyestuff which has bled from its original material article may then be absorbed, adsorbed, reacted with, or otherwise physically deposited on or associated with other articles in the same wash liquor, thus discoloring this latter item. Attempts to solve this problem have included treating the dyes or colorants so that they have a greater affinity for the dyed material. Attempts have also been made to eliminate dyestuffs discharged in the wash water. It is an object of the present invention to provide an alternative method for manufacturing a dye scavenging substrate. It is a further object of the present invention to provide an improved method for manufacturing a dye scavenging substrate, which method results in the dye scavenging substrate having improved dye scavenging capabilities. Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description of the invention and the appended claims, taken in conjunction with the accompanying drawings and this background of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background of the invention or the following detailed description of the invention. The invention provides a method for manufacturing a dye scavenging substrate which comprises the steps of: Preferably, in step b, the alkaline solution comprises a basic solution comprising water and a base, preferably NaOH. Preferably, the basic solution comprises water and the base in a respective ratio by weight of from about 1:1 to about 1:10. The alkaline solution preferably comprises the compound and the basic solution in a respective ratio by weight of from about 1:1 to about 1:10. It will be appreciated that these ratios preferably refer to the compound in solid form. Preferably, in step c, the pressure is from about 0.1 to about 1.0. Preferably, in step c, the pressure is obtained by passing the substrate between a pair of rollers, optionally pneumatically actuated rollers. It will, however, be appreciated that any other suitable type of rollers may be used. Step c may be carried out on a textile padder, e. Preferably, in step c, the substrate is passed through the rollers at a speed of from about 10 m. Preferably, in step c, an air manifold is used to maintain constant and consistent air pressure across the substrate, to enable the substrate to pick up a consistent weight of the alkaline solution containing the dye scavenging compound, therefore enabling the substrate to demonstrate a consistent and repeatable dye scavenging performance. It will be appreciated that any suitable conventional air manifold may be used. The air manifold may be provided as part of the textile padder. However, it will be appreciated that the invention is not limited thereto. Preferably, in step d, the substrate is rotated for a period of from about 24 hours to about 60 hours, more preferably from about 24 hours to about 48 hours, still more preferably from about 30 hours to about 48 hours, even more preferably from about 36 hours to about 48 hours, even more preferably from about 42 hours to about 48 hours, still more preferably about 43 or 44 or 45 or 46 or 47 or 48 hours, most preferably about 48 hours. This step of rotating the substrate is also known as the curing step. Preferably, in step d, the substrate is rotated continuously on a roller. Preferably, in step e, the acid solution comprises water and a hydrochloric acid HCl solution, preferably a 10% solution. The acid solution preferably has a pH from about 1.0 to about 2.0. Preferably, a pH probe is placed in the bath containing the acid solution in order to maintain the pH at 2. Thus, the pH probe conveniently signals the water requirement and this is dosed when required to give the correct pH automatically. Preferably, in step f, the pressure is from about 0.1 to about 1.0. Preferably, in step f, the pressure is obtained by passing the substrate between a pair of rollers, optionally pneumatically actuated rollers. The rollers are preferably nitrile rubber 70 shore hardness type rollers available from Downey Textile Machinery, details provided above. Step f may be carried

out on a textile padder, e. Preferably, in step f, the substrate is passed through the rollers at a speed of from about 10 m. Preferably, in step f, an air manifold is used to maintain constant and consistent air pressure across the substrate, to enable a consistent amount of liquid neutralizing acid solution to be squeezed from the substrate, thereby enabling the substrate to demonstrate a consistent and repeatable performance. Without limiting the invention thereto, the minimum pressure in step f is preferably higher than the minimum pressure in step c, as in step c, it is desirable to retain liquid the alkaline solution containing the dye scavenging compound, to allow the liquid to react on the substrate, whereas in step f, it is desirable to remove the liquid the acid solution used to neutralize the alkaline solution containing the dye scavenging compound, prior to drying the substrate. The drying cylinders may be drying cylinders sold under the trade name Prichard available from Downey Textile Machinery, details provided above, but it will be appreciated that the invention is not limited thereto. Optionally, after step f and prior to step g, the method may comprise one or more of the additional steps of f i - f iv: Thus, in one aspect, the method may comprise all steps a - f, f i - f iv, and g. Preferably, in steps f ii and f iv, when present, the pressure is obtained by passing the substrate between a pair of rollers, optionally pneumatically actuated rollers. Details of suitable rollers are provided above, but it will be appreciated that the invention is not limited thereto. Preferably, the pressure is approximately 0. The substrate is preferably passed through the rollers at a speed of from about 10 m. The absorbent substrate may be formed from any suitable material, and may be woven or non-woven. Examples of suitable materials include cellulosic materials such as viscose, cotton, wood pulp, paper, and mixtures thereof. The material may comprise a naturally occurring material or a synthetic material or a mixture thereof. In an embodiment, the substrate may comprise a blend of viscose and cotton in a ratio by weight in the range of from about The absorbent substrate may comprise a binder such as polyvinylacetate. A suitable substrate may be a substrate comprising viscose and cotton in a However, it will be appreciated by a skilled person that the substrate is not limited to being made from the above-listed materials, and be made from any other suitable material s, cellulosic or otherwise. It will, however, be appreciated that any other suitable dimensions may be used. The rollers used in the method of the invention are preferably nitrile rubber 70 shore hardness type rollers available from Downey Textile Machinery, details provided above. Advantages of the invention include the following, but are not limited thereto: It has surprisingly been found that using reduced pressure in step c and increased curing rotation time in step d, compared with the pressure 0. Accordingly, it is proposed that the inventors have surprisingly discovered an optimum pressure and curing time that provides the resultant dye scavenging substrate with improved dye pick-up results while also maintaining good tensile strength. It will be appreciated by a skilled person that only the pressure range in step c and curing time in step d are essential to achieve the improved results. Without wishing to be bound by theory, it is proposed that the pressure in step c is essential as it allows a sufficient amount of the dye scavenging compound provided in the alkaline solution to be retained on the substrate; and the curing time in step d is essential as it allows sufficient time for the dye scavenging compound to react with the substrate to produce superior dye scavenging results, without allowing the tensile strength to be affected. It will be appreciated by a skilled person that the method of the invention is not limited to use with a cellulosic substrate, and that any other suitable absorbent substrate may be used in order to show the improvement in dye scavenging capabilities achieved using the method of the invention. The invention will now be described in greater detail, with reference to the accompanying non-limiting examples and drawings, in which: Referring now to FIG. The method is generally carried out as follows. A roll of absorbent substrate 15 is loaded onto a roller bar not shown of the first part of the apparatus The substrate 15 is then fed via roller 20 into the bath 11 so as to pass beneath the roller 12 and out of the bath 11 to between the rollers 13, By means of pump 30, the bath 11 is charged with a basic solution as described above, via line By means of pump 31, the bath 11 is charged with a dye scavenging compound solution as described above, via line The rollers 13, 14 are set to provide a pressure of from about 0. The water impermeable material may be a water impermeable film, for example derived from regenerated cellulose, such as Cellophane trade mark, for example Cellophane available from Innovia Films Ltd, Wigton, Cumbria, United Kingdom. The substrate is preferably passed through the first and second parts of the apparatus 10 at a speed of from about 10 m. It will be appreciated that the second part of the apparatus 10 may be adapted to

include a series of two baths containing water so as to provide first and second fresh water rinses. It will be appreciated by a skilled person that the fresh water rinses do not affect the resultant substrate in any substantial way, but serve to remove the odor of the dye scavenging compound. The method may be carried out on any textile padder, for example a textile padder available from Downey Textile Machinery, details provided above, but it will be appreciated that the method of the invention is not limited to use with this particular apparatus. Example 1 A dye scavenging substrate was prepared as follows. A roll of cellulosic substrate 15 was loaded onto a roller bar not shown of the first part of the apparatus 10 FIG. The substrate 15 was passed beneath the roller 12 in the bath, then out of the bath 11 and between the pair of pneumatically actuated rollers 13, 14 set to provide a pressure of 0. The method described in this example was carried out using a textile padder available from Downey Textile Machinery, details provided above. However, it will be appreciated that the invention is not limited to use with this particular apparatus. Example 2 The following comparative test was performed in order to investigate the dye pick-up performance of a dye scavenging substrate prepared in accordance with the method of the invention. A solution of dye in water having a dye concentration of 0. The performance of substrates prepared in accordance with different methods, including the method of the invention, was investigated. The substrates used were as follows. Substrate X was placed in the dye solution for a period of 3 minutes, following which the substrate was removed and the dye concentration was measured using a spectrophotometer DR available from Hach, Willstatterstr. The process was then repeated separately for each of the remaining substrates A, B and C, using a fresh dye solution having a dye concentration of 0. These tests were repeated three times and averages taken. The results are shown in Table 1 and in FIG.