

Dec. 30, 1947.

W. A. PROELL

2,433,396

PROCESS FOR PRODUCTION OF SULFONIC ACIDS

Filed April 28, 1945

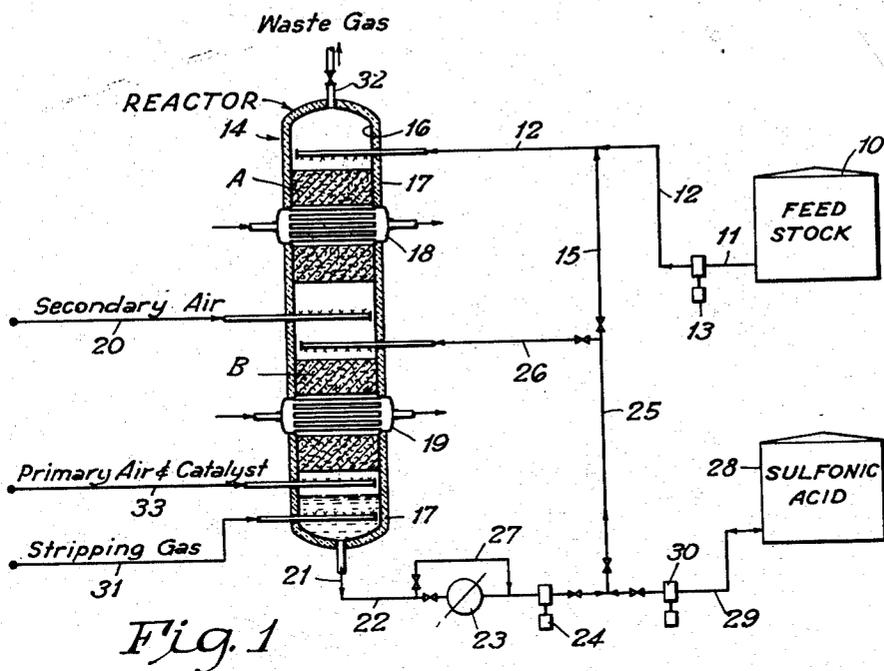


Fig. 1

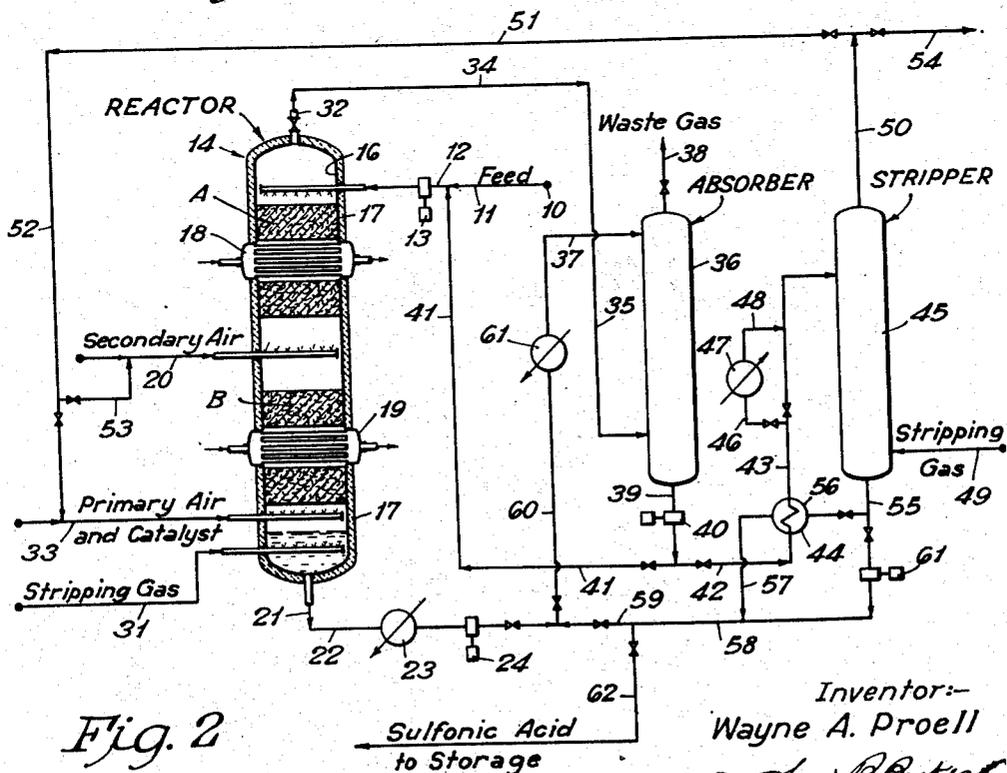


Fig. 2

Inventor:-
Wayne A. Proell
By *Sam R. Baker*
Attorney

UNITED STATES PATENT OFFICE

2,433,396

PROCESS FOR PRODUCTION OF
SULFONIC ACIDSWayne A. Proell, Chicago, Ill., assignor to Stand-
ard Oil Company, Chicago, Ill., a corporation of
Indiana

Application April 28, 1945, Serial No. 590,841

26 Claims. (Cl. 260—513)

1

This invention relates to an improved oxidation process. More particularly it relates to a process for the catalytic oxidation of organic sulfur compounds having the general formula $R_1S_nR_2$ where-
in R_1 and R_2 are organic radicals, preferably alkyl
radicals containing 1 to 5 carbon atoms, and n is
an integer having a value between 1 and 6.

It is an object of this invention to produce substantially anhydrous 100% sulfonic acids. Another object of this invention is to provide a novel two-stage oxidation process for the production of sulfonic acids. Still another object of this invention is to provide a method for oxidizing organic sulfur compounds of the above description, especially dialkyl disulfides, at a high rate to produce substantially 100% sulfonic acids. A further object of this invention is to provide an improved method for the recovery and re-use of nitrogen oxide catalysts used to promote the oxidation of organic sulfur compounds to sulfonic acids. An additional object of this invention is to provide substantially pure sulfonic acids of improved color.

I have found that the oxidation of organic sulfur compounds having the formula $R_1S_nR_2$, as above described, specifically dialkyl disulfides, with an oxidizing gas stream such as air in the presence of a catalytic quantity of a nitrogen oxide selected from the group consisting of NO , NO_2 , N_2O_3 , N_2O_4 , and N_2O_5 , proceeds smoothly and rapidly at moderate temperatures in the range of about 20° to 50° C. to produce a reaction mixture containing from about 40 to about 70% of sulfonic acids. When a concentration of sulfonic acid in the range of about 40 to about 70% is reached, the specific concentration depending on the particular feed stocks, the reaction rate is markedly reduced, for example, to about $\frac{1}{10}$ of the initial rate in many cases. In order to complete the oxidation of the organic sulfur compounds to produce substantially 100% of acids, it is necessary to increase the reaction temperature to a temperature above about 70° C. but below a temperature at which decomposition of the desired sulfonic acid begins to assume substantial proportions. This latter temperature usually lies within the range of about 120 to about 150° C. I have also found that initial high temperature catalytic oxidation of organic sulfur compounds containing less than about 40% sulfonic acids is undesirable because of low oxidation velocity and because of discoloration of the sulfonic acids which are produced. Thus, I have found that oxidation of dialkyl disulfides at 100° C. proceeds at a rate that is less than one-half the rate of

2

oxidation at 35° C., other reaction conditions than temperature remaining the same. On the other hand, oxidation of organic sulfur compounds in the presence of about 40 to about 70% of a sulfonic acid proceeds smoothly and at a high rate above a temperature of about 70° C. to yield substantially 100% sulfonic acids of desirable color.

I have also found that sulfonic acids, particularly alkanesulfonic acids containing between about 1 and about 5 carbon atoms in the molecule are excellent absorbents for the nitrogen oxide catalysts used in my oxidation process. Absorption proceeds rapidly at temperatures below about 45° C., especially below about 30° C. Thus, 95 weight percent methanesulfonic acid was found to recover most of the NO_2 present in amounts of about 1-5% by weight in admixture with nitrogen or oxygen and the rich absorbent was found to liberate NO_2 quantitatively at 100° C. without suffering oxidation or nitration. The alkanesulfonic acids are not strong dehydrating agents and resist nitration and oxidation by gas streams containing nitrogen oxides and oxygen. Moisture may be removed from alkanesulfonic acids by stripping with hot dry gases.

Feed stocks for the catalytic oxidation process of my invention comprise organic sulfur compounds having general formula $R_1S_nR_2$. The organic radicals R_1 and R_2 may be the same or different. Organic radicals differing greatly in molecular weight or chemical structure, may be present in the sulfur compounds used as feed stocks. However, the organic radicals may not be stable to oxidation under the reaction conditions employed in my process and, in that event, oxidation of both the sulfur atoms and organic radicals in the feed stock will occur. It is preferred, however, to select organic radicals which will be resistant to oxidation under the conditions employed in my process, with resultant confinement of the oxidation process to one or more of the sulfur atoms in the feed stock. Suitable oxidation resistant organic radicals are hydrocarbon radicals, especially alkyl and aryl radicals. Substituents which may or may not be oxidized under the conditions employed may or may not be present in the feed stocks, e. g., an unsaturated, substituted amino or amido, carboxyl, hydroxy, or other atoms or groups.

Suitable feed stocks include hydrocarbon disulfides, such as dimethyl, diethyl, dipropyl, dibutyl, diamyl, methylbutyl, ethylpropyl, dicresyl, dicyclohexyl, dicetyl, and dilauryl. Particularly suitable feed stocks are dialkyl disulfides containing 1 to 5 carbon atoms in the alkyl group.

3

The feed stock may be a pure compound or a mixture of compounds, optionally in admixture with substances, such as paraffinic, naphthenic, or other hydrocarbons. A preferred feed stock is a mixture consisting essentially of dialkyl disulfides, of the type obtained as a by-product in the extraction of mercaptans from petroleum distillates in the presence of an oxidation catalyst to produce a mixture of dialkyl disulfides which are separated from the caustic solution by settling or by extraction with a solvent, such as petroleum hexane, naphtha, or the like. Either the crude disulfides of a fraction thereof can be oxidized by my technique.

The extraction of petroleum distillates with caustic-solutizer solutions has been described by D. L. Yabroff and E. R. White (Ind. Eng. Chem. 32, 950-953 (1940)) and has been reviewed by V. A. Kalichevsky and B. A. Stagner ("Chemical Refining of Petroleum," revised edition, 1942, pp. 218-220). The production of disulfides by catalytic oxidation of mercaptans (present as mercaptides) in caustic-solutizer solutions has been described by J. P. O'Donnell (The Oil and Gas Journal, pp. 45-47 (July 1, 1944)). However, a brief description of caustic-solutizer extraction of mercaptan-containing petroleum fractions and conversion of the extracted mercaptans to hydrocarbon disulfides may not be amiss.

A petroleum distillate, e. g., gasoline, is intimately mixed or countercurrently extracted with a solution of caustic alkali having a concentration of the order of 5-50%, preferably about 10-25% (equivalent to 2-7 N alkali). Sodium hydroxide and potassium hydroxide are commercially convenient. In order to increase the solubility of mercaptans, especially higher alkyl mercaptans such as butyl, amyl, and hexyl mercaptans, in the caustic solution a solubility promoter or "solutizer" is added to the caustic. Suitable solubility promoters are the simple phenols, particularly cresols and xylenols, the organic acids, particularly those having 3-7 carbon atoms such as isobutyric acid, aromatic acids such as cumic acid, the alcohols, glycols, amines, and hydroxyamines. The preferred amount of solubility promoter is about 5 to about 25 weight percent of the caustic solution which is employed. The mercaptans dissolve in the caustic solution and react therewith to form mercaptides. The mercaptide containing caustic solution is separated from the petroleum distillate and regenerated by blowing with air or oxygen, usually at a temperature between 50 and 200° F., which operation oxidizes the mercaptides to disulfides and liberates the bound caustic. In order to increase the rate of oxidation of the mercaptides, a catalyst is added to the caustic solution. Suitable catalysts are phenolic compounds, e. g., naturally occurring phenolic compounds such as the tannins. The resulting disulfides can be separated from the caustic solution by settling or extraction with naphthas or the like.

A representative dialkyl disulfide mixture produced from a light naphtha by the operation of a caustic-solutizer and catalytic caustic regeneration process of the type described above boils in the range of about 115 to about 400° F. with very little material distilling below about 250° F. Fractionation analysis indicates that the predominant components are dimethyl, methylethyl, diethyl, isopropylmethyl, methylpropyl, and dipropyl disulfides. From higher boiling naphthas it is possible to recover the higher boiling disulfides which can be oxidized by my process.

4

Polysulfides having the general formula $R_1S_nR_2$ wherein R_1 and R_2 are organic radicals and n is an integer between 3 and 6 can be oxidized by my catalytic process. Numerous methods of preparing such polysulfides are known. Suitable methods, among others are described in U. S. Patents 2,237,625 and 2,237,627 and in Liebig's Annalen der Chemie 359, 81 (1907). It should be understood that the methods for making polysulfides form no part of the present invention and that polysulfides however made can be subjected to my oxidation process.

In accordance with this invention, the organic sulfur compounds are oxidized by means of a gas stream containing free oxygen, as in air, in the presence of a small catalytic quantity of one or more nitrogen oxides selected from the group consisting of NO, NO₂, N₂O₃, N₂O₄, and N₂O₅. Although all members of this group are useful, it is not intended to imply that they are equally efficacious in all respects. The organic sulfur compound is oxidized by the free oxygen and not by the nitrogen oxide or nitrogen oxides, which can be recovered unchanged upon completion of the oxidation reaction and can be re-used to catalyze the oxidation of further quantities of organic sulfur compound with free oxygen. If desired, nitrogen oxides suitable for the purposes of this invention can be generated in situ by adding a small quantity of nitric acid to the oxidation zone. The nitric acid also yields water upon decomposing in the reaction zone. Water is a necessary reactant for the production of sulfonic acids from the oxidized sulfur compounds; thus, the addition of nitric acid to the reaction zone serves two purposes, generating water and nitrogen oxide catalysts. In general, it is necessary to introduce with the feed stock less than 10% by weight of nitrogen oxides based on the total oxygen absorption, and usually the introduction of about 1 to about 5% by weight on total oxygen consumed is preferable. The nitrogen oxide catalyst can be introduced into the oxidation zone with either the organic sulfur compound feed stock or with the gas containing free oxygen, or with both, or may be introduced separately. The nitrogen oxide catalyst may be recovered from effluents passing from the oxidation zone and recycled to the same or a different oxidation zone.

The production of sulfonic acids from the sulfur compounds used as feed stocks in the oxidation process of this invention requires water as a reactant. Ordinarily I prefer to add, an amount of water not in substantial excess of that required to combine with the oxidation products to produce sulfonic acids, i. e., one mol of water per mol of disulfide used in the oxidation reaction mixture. Accordingly, I can readily obtain substantially anhydrous sulfonic acids, e. g., 90 to 100% sulfonic acids. The anhydrous sulfonic acids are more desirable products than hydrated sulfonic acids or sulfonic acids in water solution, since, for many uses, the anhydrous acid is required. By adding no more, and preferably less, than the amount of water required to yield sulfonic acids, it is possible to obviate the expensive operations attendant on concentrating and drying hydrous sulfonic acids. Ordinarily, a suitable proportion of water is within the range of about 1 to about 20 weight percent based on the feed stock.

It is convenient and preferable to maintain the sulfur compound feed stock in the liquid phase during the oxidation reactions. This result can be readily attained by proper control of the pressure on the oxidation zones. Pressures in the

range of about 5 to about 100 pounds per square inch are convenient and generally sufficient. Other reaction conditions being constant, the rate of oxidation will increase with increasing partial pressures of oxygen in the oxidation zones. When using air or other gases containing relatively small proportions of oxygen, e. g., flue gases containing free oxygen, it is desirable to operate the oxidation zones under pressure to increase the oxygen concentration therein. The oxidation reactions may, however, be effected in the vapor phase, especially when relatively low-boiling sulfur compound feed stocks, e. g., feed stocks boiling below about 245° F., are employed.

The reaction period depends on the particular feed stock and other reaction variables. It can, in each case, be determined by simple experiment.

My novel oxidation process may be carried out batchwise, continuously, or semi-continuously. The oxidation process may also be effected in a number of stages with or without product separation between stages. The oxidation reactions may be effected in conventional reaction kettles or autoclaves, or in tubular convertors or contacting towers. A suitable form of reactor is a vertical tower provided with contacting means such as bubble cap trays or with packing such as ceramic bodies or fiber glass mats. Countercurrent contacting of liquid sulfur compound feed stock and the oxidizing gas stream proceeds efficiently in the types of reaction tower just described; the liquid feed is passed downwardly through the tower against a rising stream of oxidizing gas, all of which may be admitted at a point near the bottom of the tower or, preferably, aliquot portions of which are introduced at vertically spaced points along the tower. A tubular reactor equipped for spaced injection of oxidizing gas into a flowing stream of liquid or vaporized feed stock and oxidation products may also be employed; a reactor of this type permits fine control of the extent of oxidation.

The various individual oxidation products may be recovered from the reaction mixture by conventional means which will vary with the nature of the individual reaction product mixture. Such methods as extraction with solvents, fractional crystallization, distillation, particularly vacuum distillation, and the like may be used. Products and catalyst carried out of the oxidation zone by the effluent oxidizing gas stream may be recovered by cooling, absorption, or other processes. Partial oxidation products, when desired, and catalyst may be recycled to the oxidation zone.

The following example is set forth with the intention of illustrating, but not limiting, my invention.

Example I

Dimethyl disulfide was passed downwardly through a glass tower packed with glass beads against a countercurrent flow of oxygen. The oxygen injection rate was 0.5 cubic feet per hour per 100 grams of dimethyl disulfide. The reaction temperature was maintained at 35° C. and the reaction period was five hours. Nitrogen oxides derived from nitric acid were used as catalysts, the concentration of nitrogen oxides being about 6%. Dimethyl disulfide containing methanesulfonic acid was withdrawn from the bottom of the oxidation reactor and recycled to the top for further oxidation. It was observed that when the acid strength reached about 70%, the oxygen absorption efficiency in the reactor dropped with-

in ten minutes from an average value of 50% to 15% in spite of constant catalyst feed. It was found that by increasing the temperature in the oxidation reactor to 100° C. by the use of a steam jacket, the oxygen absorption efficiency increased to 95% average until substantially complete oxidation of the dimethyl disulfide feed stock was achieved. A pale, reddish-brown colored product assaying 97% by weight methanesulfonic acid was thus obtained. Attempts to oxidize dimethyl disulfide initially at 100° C. showed that the oxygen absorption efficiency was only 20 to 30%. It was also observed that initial high temperature oxidation on the raw disulfide feed stock resulted in the excessive catalyst loss from the top of the oxidation reactor and produced a deeply colored product.

The accompanying figures illustrate my invention but are not intended unduly to limit the same. Figure 1 illustrates equipment for effecting two-stage oxidation of an organic sulfur compound and absorption of nitrogen oxide catalysts, all the operations being effected in one reaction tower. In Figure 2, two-stage oxidation is effected in one reactor tower and nitrogen oxide catalysts are absorbed in an extraneous absorber and may be regenerated in an extraneous stripper for recycle to the oxidation reaction tower.

Referring to Figure 1, feed stock for example a dialkyl disulfide, is pumped from storage tank 10 through line 11, pump 13, and line 12 into oxidation reactor 14. A substantially pure (100%) sulfonic acid, preferably a sulfonic acid identical with that produced in the oxidation process is pumped via line 15 to join the feed stock in line 12. The amount of sulfonic acid recycled through line 12 may be sufficient to yield a mixture containing between about 40 and about 90% sulfonic acid passing into reactor 14. As shown, reactor 14 comprises a shell 16 provided with insulation or lagging 17 and internal heat exchangers 18 and 19 provided with headers and tubes. In order to secure intimate contacting of the feed stocks and oxidizing gas streams in the reactor, packed contacting zones A and B are provided. Any suitable packing materials may be used in these zones, for example, ceramic bodies, glass beads, glass mats, glass wool and the like. Zone A is maintained at a temperature in the range of about 20 to about 50° C. In zone A the feed stock flows downwardly through the packing material and heat exchange surfaces against a counterflow of oxidizing gases, derived principally from zone B. However, additional oxidizing gases, e. g., secondary air, may be introduced into zone A via line 20. The operating conditions are so adjusted that a small amount of oxidation takes place in zone A, but its chief function is to strip out nitrogen oxides such as NO and NO₂ from the gases passing into zone A from zone B. The oxidation conditions in zone A are so adjusted that the product flowing out of the bottom of zone A contains between about 40 and about 90% sulfonic acids by weight.

Zone B is maintained at a temperature within the range of about 70 to 150° C., preferably between about 70 and 120° C., for example, 100° C. Effluents from zone A pass downwardly through the packing material and heat exchange surfaces of zone B against a counterflow of oxidizing gases and catalysts introduced via line 33. The water required in the process may also be introduced via line 33. In zone B, oxidation of the feed

stock may be virtually completed in one pass, or the operating conditions may be so adjusted as to provide for multi-pass operation through this zone to achieve substantially complete oxidation. Recycling of sulfonic acids through zone B may be effected via lines 21 and 22, cooler 23, pump 24, and lines 25 and 26, valves in the various lines being suitably set to effect this mode of operation; the cooler 23 may be by-passed by valved by-pass line 27. Substantially pure sulfonic acids may also be introduced into zone B from storage vessel 28 via line 29, pump 30, and lines 25 and 26 by suitable adjustment of the valves therein. In order to avoid loss of nitrogen oxide catalyst with oxidation products leaving reactor 14 by line 21, a stripping gas is introduced into the reactor via line 31. A suitable stripping gas is air or oxygen which simultaneously strips and, to some extent, reoxidizes the nitrogen oxide catalyst which is then further utilized in zones B and A. However, inert stripping gases such as nitrogen, substantially deoxygenated flue gases, carbon dioxide or steam may also be used. When substantially complete oxidation of the feed stock has been effected, stripped products are passed from the bottom of reactor 14 via lines 21 and 22, cooler 23, pump 24, through line 29 to a storage vessel 28 for substantially pure sulfonic acids. Waste gases comprising largely nitrogen (when air is used as the oxidant in the oxidation process) and small proportions of water vapor, nitrogen oxides, etc., are removed from reactor 14 via valved line 32 and may be processed to recover any materials of value contained therein, or discarded from the system.

In the oxidation of dialkyl disulfides, e g., dimethyl disulfide, in accordance with the above described process, the raw product generally consists of a pale orange to brown oily liquid. This material usually assays about 93% sulfonic acid, 1-3% sulfuric acid, 3% water and 2% of organic material, chiefly unoxidized disulfides. Blowing this raw product with air or subjecting it to vacuum distillation removes the water and most of the unreacted disulfides as a distillate and yields a finished acid assaying about 97% sulfonic acid. The sulfonic acids thus produced are completely soluble in water with only a trace of turbidity.

It will be understood that, although reactor 14 is shown as containing both zones A and B, these zones can be situated in different towers. In addition, although a fixed bed of contacting or packing material is shown in Figure 1, it should be understood that I may use moving beds of contacting material or fluidized solid contacting material as is well known in the art of catalysis, especially in the art of hydrocarbon conversions.

In Figure 2, the same numerals have been used to indicate the same parts as in Figure 1. Thus, as in Figure 1, feed stock passes from source 10, lines 11 and 12, and pump 13 into reactor 14 thence downwardly through reaction zones A and B and out of the reactor via line 21. However, in Figure 2, the operating conditions are so adjusted that substantial oxidation is effected in zone A and most of the absorption of nitrogen oxide catalysts and, in some cases of unconverted organic sulfur compounds, carried out of the reactor by valved line 32, is effected in a zone external to the reactor. The feed stock to zone A contains between 0 and about 40% of sulfonic acids and the oxidation temperature and time are adjusted to yield an effluent containing between about 40 and about 90% sulfonic acids by

weight. Suitable temperatures lie in the range of about 20 to about 45° C.

A gas stream passes overhead from reactor 14 via valved line 32 and lines 34 and 35 into the lower portion of absorber 36. In the absorber, the gases containing nitrogen oxides are washed with a counterflow of cool sulfonic acid introduced via line 37. It is desirable to use a sulfonic acid produced in the oxidation process as the absorbent medium. The absorber is operated at a temperature not in excess of about 45° C. and preferably at temperatures in the range of about 0° C. to about 30° C. Waste gases are removed from the absorber via valved line 38. The enriched absorbent is removed from the absorber via line 39 and pump 40 and may be cycled directly to line 12 to intermingle with the feed stock passing into reactor 14 via valved line 41. Alternatively the enriched absorbent medium is passed by valved line 42 through heat exchanger 44 in line 43 to a stripper 45. Further heat may be imparted to the enriched absorption medium by by-passing it from line 43 into valved line 46 to heater 47 and thence back to line 43 by line 48. In the stripper 45, the enriched absorption medium is subjected to a temperature sufficient to volatilize a substantial portion or all of the nitrogen oxides and in some cases, organic sulfur compounds at a lower state of oxidation than sulfonic acids. Suitable stripping temperatures fall within the range of about 70 to about 110° C. In order to facilitate stripping it is desirable to introduce a stripping gas, for example, air, oxygen, nitrogen, carbon dioxide, steam, or the like through line 49. A gas stream containing the desorbed nitrogen oxides passes overhead from stripper 45 through valved lines 50 and 51 to valved line 52 whence all or a portion may be passed through line 53 into the secondary air line 20 or into line 33 to join the stream of primary air and catalyst. If desired, part of the stripped gases may be removed from the system by valved line 54. The lean absorbent medium is passed from the bottom of stripper 45 by means of valved lines 55 and 56 through heat exchanger 44 and thence through lines 57, 58, 59, 60, and cooler 61 and line 37, for recycle to absorber 36. Alternatively all or a portion of the lean absorbent may be passed through lines 55 and pump 61 into line 58 for recycle to the absorber 36 via lines 59, 60, and cooler 61, and line 37 into absorber 36. Concentrated sulfonic acids may be withdrawn either from the reactor or from the absorption system via valved line 62. Concentrated sulfonic acids for use as an absorption medium in absorber 36 may be withdrawn from reactor 14 through lines 21 and 22, cooler 23, pump 24, line 60, cooler 61 and line 37 into absorber 36.

As in Figure 1, it will be understood that reactor 14 can be separated into two distinct reaction towers, each of which will contain one of the reaction zones A or B. Furthermore, the fixed bed of contacting material may be replaced by a moving or fluidized bed.

The concentrated, substantially pure alkanesulfonic acids produced by the process of this invention are strong organic acids, extremely stable to hydrolysis, either under acidic or basic conditions. In addition, alkanesulfonic acids are extremely resistant to oxidation and nitration by nitrogen oxides, exert only a feeble dehydrating action, and have low volatility. Their odor is mild and can be eliminated without difficulty by suitable means such as distillation. A number

of applications for alkanesulfonic acids, particularly those containing 1 to 5 carbon atoms in the molecule, is set forth below.

The common olefins can be hydrated by sulfuric acid, but the oxidizing and dehydration action of this acid causes the formation of undesirable by-products and sludge. Alkanesulfonic acids permit hydration without acid destruction. It was found that 1- and 2-pentene react with butanesulfonic acid to give the ester. Hydrolysis of the ester gave a low-boiling complex mixture of hydrocarbons and oxygenated compounds. Acid recovery by removing water from the dilute acid was easily accomplished, the recovered acid being lighter in color than the original.

The direct hydration of propylene by steam over a sulfuric acid catalyst is not feasible because the acid breaks down to SO₂ and carbon deposits on the catalyst. This same process was tried using a silica gel or charcoal support for a butanesulfonic acid catalyst. A small yield (5%) of oxygenated material, apparently diisopropyl ether, was obtained. It is worth noting that the catalyst did not char, discolor, or break down when maintained for several hours at 270° F.

The acids have a mild polymerizing and alkylating action. Particularly, alkanesulfonic acids can be used as catalysts for the alkylation of aromatics with olefins or other well-known alkylating agents.

Because of the extreme stability of the low molecular weight sulfonic acids to hydrolysis, and their strength as acids, they can be used as esterification catalysts, particularly where the material being esterified or hydrolyzed is valuable, sensitive, or reactive.

A brief test on cellulose showed dilute butanesulfonic acid to be an effective hydrolysis catalyst, converting the cellulose to a starchy paste with no discoloration. Sulfuric acid gave faster hydrolysis but gave a discolored brown product.

Because of their high solubility and corrosivity, the alkanesulfonic acids can be used as pickling agents. The sulfonic acids attack metals uniformly and slowly. Aluminum is given a satin finish by pickling.

Alkanesulfonic acids containing 1 to 5 carbon atoms in the molecule can be used as electrolytes in electroplating metals, particularly nickel and lead. When used in electroplating or electrorefining, the acid is used in the form of a metal salt, and it may be used in mixture with alkali metal salts of the acid or in admixture with the acid itself, depending on the desired cell conductivity and pH.

It is known in the art that both lead and nickel can be satisfactorily plated from solution. However, in the case of lead, only a few suitable electrolyte salts are known since the common salts of lead, e. g., sulfate and chloride are insoluble, or unsuitable for other reasons. Thus, lead plating solutions are preferably acidic and lead plating is done in such media as lead fluoborate or lead fluosilicate solutions. Such solutions are expensive and quite toxic due to volatile acid (HF). It has been proposed to use lead sulfamate; indeed, electrolysis of sulfamate solutions gives a bright, dense coat. But sulfamate solutions hydrolyze rapidly at 50-80° C. and deposit lead sulfate sludge. I have found that the lead sulfonates are water soluble and contain ionic lead. Thus lead n-butanesulfonate will dissolve to the extent of 39.6 grams per 100 grams water at 25° C. It is more soluble in warm water. The lead salt is readily purified and can be heated for 24

hours at 100° C. in aqueous solution without any hydrolysis. The solubility of lead ethanesulfonate in water is 67.3 grams for 100 grams of solution. For these reasons, alkanesulfonic acids are excellent media for the electrodeposition of lead.

It is also known in the art that nickel is difficult to electroplate because it tends to become passive in conventional sulfate baths and fails to give anodic attack. I have found that even in the absence of an electrical current, nickel alloys of all sorts (excepting 18-8 stainless steel) are rapidly attacked by hot concentrated alkanesulfonic acids. Alkanesulfonic acids can be used in nickel electroplating baths and also in chrome plating.

A prime consideration in electroplating is the ability of a given anion to retain stability in all pH's. The alkanesulfonic acids such as methane-, ethane-, and butanesulfonic acids are stable in alkali, acid, or neutral solutions, both hot and cold.

Alkanesulfonic acids having from 1-10 carbon atoms in the molecule, for example, 1 to 5 carbon atoms, can also be used as tanning sours, laundry sours, and photographic sours. They can be used in weed killing compositions, together with other toxic ingredients or carriers. They can also find application as catalysts in phenol-aldehyde resinification reactions.

The lower alkanesulfonic acids have shown a marked capacity for absorbing nitrogen oxides, even in low concentration, from gas streams. Fields of application for this property include the recovery of fumes from salt cake manufacture, NO₂ removal from products of the air oxidation of ammonia, fumes recovery in the pickling of metals with nitric acid and the removal of nitrogen oxides from manufactured gases, for example, manufactured fuel or illuminating gases, wherein nitrogen oxides serve, undesirably, as olefin resinification catalysts.

The lower alkanesulfonic acid can be used as substitutes for the so-called Twitchell reagents used in fat splitting. They can also find application in oil well treating as a substitute for, or adjunct to, other strong acids now used. The ammonium salts of the lower alkanesulfonic acids, ammonium methanesulfonate, can be used as fire retarding compositions.

Alkanesulfonic acids can also be used as selective solvents. Thus, extraction of cleaners' naphtha having a refractive index (n_D^{20}) of 1.4150 with n-butanesulfonic acid yielded an extract fraction having a refractive index (n_D^{20}) of 1.43 to 1.444. The refractive index of (n_D^{20}) of the raffinate was 1.4148.

Other uses for the lower alkanesulfonic acids will, no doubt, suggest themselves to those skilled in the art.

The invention above described makes available a plentiful supply of substantially pure alkanesulfonic acids having from 1 to 5 carbon atoms in the molecule by a cheap and efficient process which is commercially feasible. Having thus described my invention, what I claim is:

1. The process for producing a sulfonic acid which comprises oxidizing an organic sulfur compound having the formula R₁S_nR₂ wherein R₁ and R₂ are hydrocarbon radicals and n is an integer having a value between 1 and 6 at a temperature above about 70° C. with a gas containing free oxygen and a catalytic quantity of a nitrogen oxide selected from the group consisting of NO, NO₂, N₂O₃, N₂O₄, and N₂O₅, and water, the oxidation being effected in the initial presence of at

least about 40% of an alkane-sulfonic acid, and recovering a sulfonic acid so produced.

2. The process of claim 1 wherein the sulfonic acid initially present is identical with a sulfonic acid being produced in said process.

3. The process of claim 1 wherein the organic sulfur compound is a dialkyl disulfide.

4. The process of claim 1 wherein the organic sulfur compound is dimethyl disulfide.

5. The process of claim 1 wherein R_1 and R_2 are alkyl radicals containing 1 to 5 carbon atoms.

6. The process of claim 1 wherein the organic sulfur compound is a mixture of dialkyl disulfides boiling in the range of about 115 to about 400° F. containing predominantly 4 and 5 carbon atoms in the molecule.

7. In a process for producing a sulfonic acid which comprises oxidizing an organic sulfur compound having the formula $R_1S_nR_2$ wherein R_1 and R_2 are hydrocarbon radicals and n is an integer having a value between 1 and 6, the oxidation being effected by the reaction of said sulfur compound with a gas containing free oxygen, water and a catalytic quantity of a nitrogen oxide selected from the group consisting of NO , NO_2 , N_2O_3 , N_2O_4 , and N_2O_5 , the steps comprising subjecting said sulfur compound in a first oxidation stage to a temperature between about 20° C. and about 50° C. until the sulfonic acid content of the oxidation reaction mixture attains a value between about 40% and about 70%, subjecting the oxidation reaction mixture produced in the first oxidation stage to oxidation in a second oxidation stage at a temperature between about 70° C. and about 150° C. for a period of time sufficient to increase the sulfonic acid content of the resultant mixture to at least 90%, and recovering sulfonic acids so produced.

8. The process of claim 7 which comprises separating a gas stream containing a nitrogen oxide from the first oxidation stage, subjecting said gas stream to absorption in a liquid medium containing sulfonic acids, desorbing nitrogen oxides from said liquid medium and passing the desorbed nitrogen oxides to the second oxidation stage.

9. The process of claim 7 wherein the substantially 100% sulfonic acids produced in the second oxidation stage are stripped of nitrogen oxides, and said nitrogen oxides are recycled to the second oxidation stage.

10. The process of claim 7 wherein the substantially 100% sulfonic acids produced in the second oxidation stage are stripped of nitrogen oxides, and said nitrogen oxides are recycled to the first oxidation stage.

11. The process of claim 7 wherein the organic sulfur compound is dimethyl disulfide.

12. The process of claim 7 wherein the organic sulfur compound is dialkyl disulfide.

13. The process of claim 7 wherein the organic sulfur compound is a mixture of dialkyl disulfides boiling in the range of about 115 to about 400° F. containing predominantly 4 and 5 carbon atoms in the molecule.

14. The process of claim 1 wherein the organic sulfur compound is a disulfide.

15. The process of claim 7 where the organic sulfur compound is a disulfide.

16. The process of claim 1 wherein the temperature is above about 70° C. but not in excess of about 150° C.

17. The process of claim 1 wherein R_1 and R_2 are alkyl radicals at least one of which is primary and n is 2.

18. The process of claim 1 wherein R_1 and R_2 are primary alkyl radicals and n is 2.

19. The process of claim 1 wherein R_1 and R_2 are alkyl radicals at least one of which is secondary and n is 2.

20. The process of claim 1 wherein R_1 is a primary alkyl radical, R_2 is a secondary alkyl radical and n is 2.

21. The process of claim 1 wherein a nitrogen oxide is produced in the reaction zone by decomposition of nitric acid.

22. The process of claim 7 which comprises the additional steps of separating a gas stream containing a nitrogen oxide from the oxidation process, subjecting said gas stream to absorption in an alkanesulfonic acid containing 1 to 5 carbon atoms in the molecule and passing said alkanesulfonic acid containing an absorbed nitrogen oxide to said first oxidation stage.

23. The process for producing a sulfonic acid which comprises oxidizing a dialkyl disulfide at a temperature above about 70° C. but not in excess of about 150° C. with a gas containing free oxygen and a catalytic quantity of a nitrogen oxide produced in the reaction zone by decomposition of nitric acid, and water, the oxidation being effected in the initial presence of at least about 40% of an alkanesulfonic acid identical with a sulfonic acid being produced in the oxidation process, and recovering a sulfonic acid so produced.

24. In a process for producing a sulfonic acid which comprises oxidizing a dialkyl disulfide, the oxidation being effected by the reaction of said dialkyl disulfide with a gas containing free oxygen, water and a catalytic quantity of a nitrogen oxide produced in the reaction zone by decomposition of nitric acid, the steps of subjecting said dialkyl disulfide in a first oxidation stage to a temperature between about 20° C. and about 50° C. until the sulfonic acid content of the oxidation reaction mixture attains a value between about 40% and about 70%, subjecting the oxidation reaction mixture produced in the first oxidation stage to oxidation in a second oxidation stage at a temperature between about 70° C. and about 150° C. for a period of time sufficient to increase the sulfonic acid content of the resultant mixture to at least 90%, and recovering sulfonic acids so produced.

25. The process of claim 1 wherein the nitrogen oxide is NO_2 .

26. The process of claim 7 wherein the nitrogen oxide is NO_2 .

WAYNE A. PROELL.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
908,935	Tschunkur et al.	May 16, 1933
1,925,191	Keller	Sept. 5, 1933
2,187,338	Werntz	Jan. 16, 1940
2,187,339	Werntz	Jan. 16, 1940
2,204,210	Farlow	June 11, 1940