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SULPHONATES

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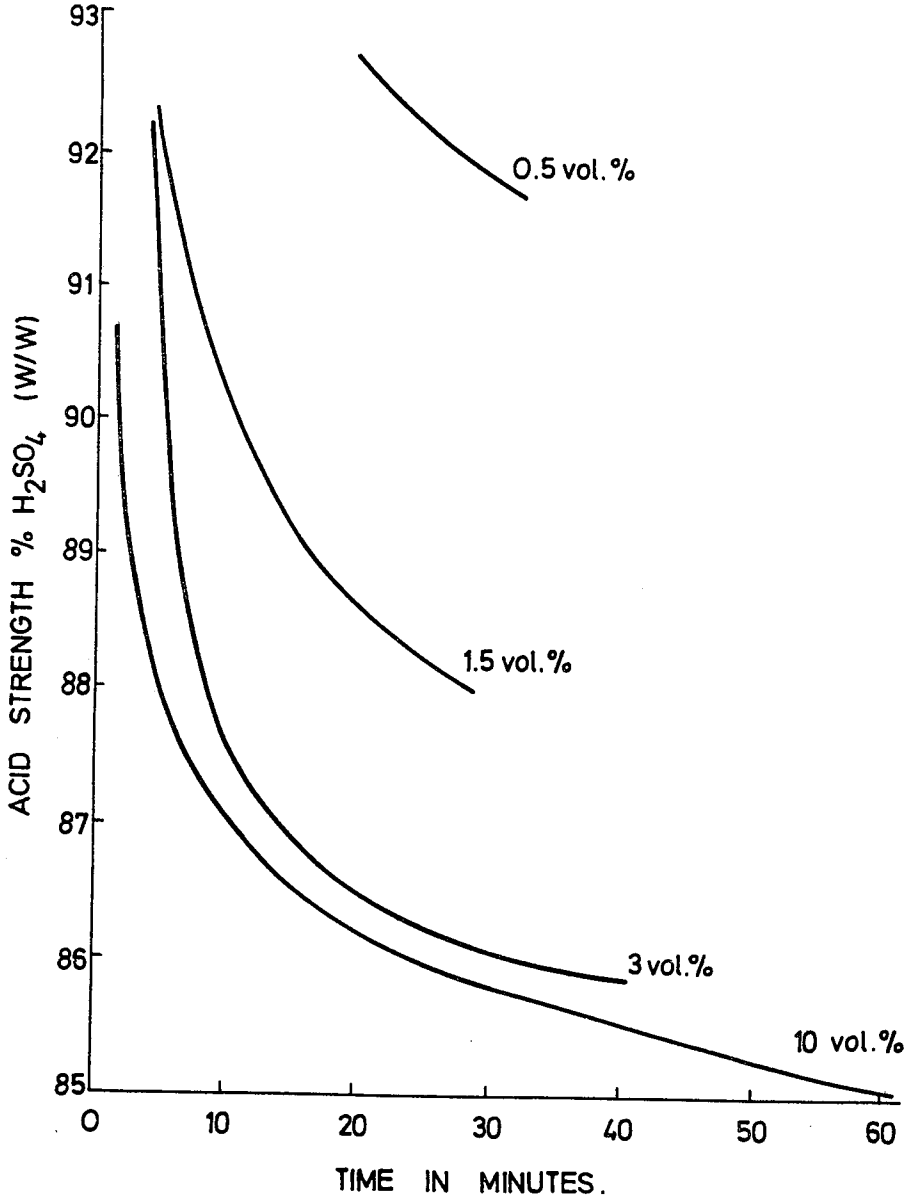

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SULPHONATES

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ABSTRACT OF THE DISCLOSURE

The invention concerns a process for the purification of olefins from which olefin sulphonates having an improved colour can be obtained. The process involves treatment of an olefin, especially a commercial alpha-olefin, with sulphuric acid under specific conditions, followed by treatment with an earth.

This invention relates to sulphonates of olefins, especially of commercial alpha-olefins of carbon chain length 10–22, to a process for preparing them, and to their use in detergent compositions.

Useful actives for detergent compositions can be prepared by allowing SO_3 to react with olefins of chain lengths ranging from C_{10}–C_{22} with subsequent hydrolysis/neutralisation to the salt. Unfortunately, in many cases, the sulphonate derived from commercially available alpha-olefins is too highly coloured to be acceptable for use in finished detergent products.

Commercially available alpha-olefins, especially those which are derived from the cracking of petroleum hydrocarbons, known as cracked wax olefins, tend to be straw coloured and to contain not only coloured impurities but also compounds which may be colourless in themselves but which give rise to highly coloured compounds on reaction with SO_3. These intensely coloured compounds which appear to be present in the sulphonate product in very small concentrations are thought to be polysulphonated polyenes, possibly derived by oxidation and subsequent sulphonation of the hydrocarbon chain of some of the more reactive impurities. They are believed to account for much of the sulphonate colour. Conjugated polyenes of the type $R—(CH=CH)_n—R$ are known to be highly coloured when $n=6$. The coloured compounds obtained in the sulphonation of commercial alpha-olefins are not necessarily linear and may well be derived from the non-straight chain impurities. They might also be formed from olefin dimers or from fragmented olefins, but the major colour body precursors are believed to be polyenes and particularly the cyclic dienes.

The situation is complicated by the lack of a simple test by which any particular olefinic raw material can be classified as being likely to yield a sulphonate of good (i.e. acceptable) or unacceptable colour in detergent compositions. An olefin feed stock which appears water-white can, nevertheless, on sulphonation, give a sulphonate of too high a colour. In consequence, the olefin has to be test-sulphonated before it is known if it is suitable for detergent sulphonate production. Such sulphonation is best carried out on a pilot plant scale as representative of the envisaged large-scale processing. This is a time-consuming operation and requires large quantities of olefin.

As has been stated above, when the commercial alpha-olefins are used to prepare alkali metal sulphonates for use in detergent compositions, the colour level of these

sulphonates is too high. It is therefore necessary to reduce the colour level of the olefin sulphonates.

Whilst it has been common practice in the detergent industry to improve the colour of sulphonated hydrocarbons by bleaching, it is not possible to improve the colour of these sulphonates in many cases, particularly those of cracked wax olefins. Bleaching, even with unusually large quantities of bleaching agent does not effect the requisite colour improvement. This has precluded hitherto the use of the cracked wax olefins for detergent sulphonates.

The present invention is concerned with a means for producing acceptably coloured sulphonates from commercial olefins. In particular, it is concerned with a means of removing the undesirable colour-forming compounds from the olefins before sulphonation, so that the final sulphonate product has an acceptable colour. The invention is applicable to cracked wax olefins as such and is particularly useful therewith since the combined cost of these olefins and the purification process of this invention is much less than the cost of the other commercially available olefins made from ethylene by a Ziegler polymerisation process. The latter type of commercial olefins generally give better coloured sulphonates but if the process steps of this invention are employed some of these Ziegler olefins can be purified thereby.

The cracked wax olefins contain typically 85–95% straight chain alpha-olefin, the remainder being a mixture of many hydrocarbon types, including branched, cyclic, internal olefins and smaller quantities of dienes. The Ziegler olefins similarly contain 85–90% straight chain alpha-olefins but the remainder is mainly a mixture of 2-alkyl-1-olefins. Whilst the Ziegler olefins are usually water-white, nevertheless on sulphonation, colour can develop, and the product is then unsuitable for detergent compositions.

It has been proposed to purify the olefins by passing them over absorbents, such as silicas, aluminas or clays. Washing the olefins with solvents are also prior proposals. Whilst these methods are recognised as removing the more polar or the more basic hydrocarbons, they do not always provide sufficient purification to produce an olefin which is suitable for sulphonation for detergents.

It has also been proposed to improve the visible colour of olefins by treatment with sulphuric acid. In contrast to the treatment of other hydrocarbons the conditions for treatment of olefins with sulphuric acid are extremely critical since the olefins themselves react with sulphuric acid. It has also been proposed to purify commercial olefins to render them suitable for free radical reaction by way of sulphuric acid treatment but this prior proposal included very many processing steps, viz, after the contacting of the acid and olefin the mixture is allowed to settle and the acid layer removed. The olefin layer is then neutralised with base and then washed repeatedly until the water washing is neutral. The washings are necessary to prevent the olefin reacting further with entrained acid, to prevent isomerisation and sulphation and to prevent corrosion of equipment in the subsequent steps. After a drying step the olefins are very often re-distilled to remove any condensed by-products of the treatment and thus to complete their purification. Although the olefins so obtained by this prior proposal have possessed some improved properties, the treatment has often resulted in the isomerisation of some of the olefins to internal olefins. For some uses, this isomerisation is undesirable. Consequently this purification proposal is not really satisfactory in that it involves a plurality of operating steps, and since some of the products of the acid treatment are highly surface-active emulsions are formed particularly in the caustic and water washing stages,

which necessarily cause loss of olefin and give rise to problems of processing and storage.

The present invention, which provides a process for the treatment of olefins prior to sulphonation to make possible the production of an alkali metal sulphonate of a good colour which is suitable for inclusion in a detergent composition, is appreciably simpler than the foregoing proposed process. It completely eliminates the many washing steps and the distillation step and it does not isomerise the olefin. Indeed, in many cases, the present process renders unnecessary a bleaching step for the sulphonates so prepared, and this, as will be apparent to those skilled in the art, is a considerable advantage.

Accordingly, the present invention provides a process for the purification of olefins which comprises subjecting the olefin to treatment with sulphuric acid under conditions which do not give rise to olefin sulphation or isomerisation to yield an acid layer and an olefin layer, phase separation of the layers and treatment of the olefin layer with an absorbent.

The treatment with sulphuric acid should be such as to avoid, substantially isomerisation, particularly when alpha-olefins are to be purified since retention of the olefinic double bond in the alpha-position ensures that the sulphonate group adds itself to the end of a long chain, a positioning which is desirable in detergent actives. It should also avoid polymerisation and formation of the esters of sulphuric acid. By the reaction of the sulphuric acid and the alpha-olefins according to this invention, only 1% at most of high boiling material based on the weight of the starting olefin remains in the olefin layer at the end of the acid absorbent treatment. The acid treatment removes the more powerful colour precursors, which are believed to be, in the case of the cracked wax olefins, the more basic alkyl-cyclopentadienes, and the open chain conjugated dienes.

It has now been found that sulphation of the olefin should be avoided because the sulphated products which are mainly a mixture of alkyl hydrogen sulphate and dialkyl sulphate are detrimental to good colour and also to future processing of the olefin. Some, for example the dialkyl sulphates, cannot be removed from the olefin by water washing since they are truly soluble in the olefin. A test is described below by which acid treatment conditions according to the invention suitable for any given olefin can be established. It will be realised that commercial olefins, especially cracked wax alpha-olefins vary considerably from batch to batch, as between suppliers, and as between different carbon chain cuts. The significance of the dialkylsulphate formation in the criticality of the conditions for effective acid treatments of olefins has not hitherto been appreciated. Use of the test enables any olefin to be successfully treated by the process of the invention to yield satisfactory sulphonates.

The sulphuric acid strength is conveniently 70–98% by weight H_2SO_4, preferably 80–90Z. 86Z is usually the preferred acid strength for reasons which will be given later. It is advantageous that sulphuric acids of this strength are not corrosive to mild steel, a convenient structural material. The amount used should lie within the ratios olefin:acid volumes of 100:0.1 to 4:1. It may be convenient to recycle the acid sludge, in which event, the olefin:acid ratio may be as high as 1:1. The temperature at which the acid treatment is carried out can be from 0–100° C. preferably 10–50° C. provided of course that the temperature is greater than the freezing points of the acid and the olefin. The time of contact is of the order of 0.5–60 minutes, preferably 2–20 minutes. The olefin and acid conveniently are stirred together.

Although the range of acid strength suitable for the treatment can be wide, the combination of acid strength and contact time, quantity of acid and temperature is critical in order to confine the reaction to the compounds which cause high sulphonate colour in the crude olefin, and to avoid excessive occurrence of reaction of the alpha-olefins themselves. When the stronger acids are used, short contact times, lower temperature and smaller quantities of acid are needed to avoid occurrence of sulphation and isomerisation. On the other hand, the weaker acids need longer contact times and higher temperatures, together with a larger ratio of acid:olefin, to enable sufficient reaction with the undesirable impurities to occur.

The above referred-to test will now be described. A selected quantity of the olefin to be purified is treated with sulphuric acid of strength lying within the range 85–93% H_2SO_4 (w./w.) at concentrations of 0.5 to 10 vol. percent for a time of up to 50 minutes. The mixture is allowed to phase separate and the resulting olefin layer is subjected to a standardised earth treatment, viz, 1×6% type 237 fuller's earth is mixed with the olefin layer for 8 minutes with settlement for the necessary period for clarity. The infra red spectrum of the resulting olefin is then recorded, the absorbance being measured at 6.25 and 8.4μ to provide a measure of sulphation, and at 10.1 and 10.4μ to provide a measure of olefin isomerisation.

For olefins suitable for detergent sulphonates, the acid treating conditions should be such that the ratio of absorbance at 8.4μ to that at 6.25μ is preferably zero but in any case no greater than 0.25, and to avoid olefin isomerisation, the acid treating conditions should not allow the ratio of absorbances at 10.4 to 10.1μ to be greater than that in the starting olefin. When the ratio of absorbance at 8.4μ to that at 6.25μ lies between 0.15 and 0.25, colour improvement is effected, but the final detergent sulphonate product may contain an unduly large amount of non-detergent organic matter. In this case, it may be necessary to remove this by, for example, solvent extraction in order to produce a product satisfactory for detergent use.

As an illustrative example a cracked wax C_{15-18} olefin (ex Chevron Chemical Co.) was acid treated using different values for acid strength, quantity and contact time and the resulting olefin layer subjected to the standardised earth treatment of the test.

The curves in the accompanying figure graphically present the results; all conditions of acid treatment lying beneath the respective curves represent treatments which yield a sulphonate which is satisfactory for use in detergent compositions. The areas beneath each of the respective curves represent the optimum conditions, i.e. at which no sulphation or isomerisation occurred or, expressed in another way where absorbance at 8.4μ was zero, and at 10.4 microns identical with that of the starting olefin.

Conditions represented by points above the respective curves spoil the olefin from the point of view of producing acceptably coloured olefin sulphonates. They also result in handling difficulties and yield losses in the adsorbent treating stage as described later.

It will be appreciated that the curves in the figure do not necessarily apply to any other batch of olefins even to a nominally identical batch whose identity is supported by examination by infra red analysis and by gas chromatography. As a practical measure, therefore, it is preferable to employ acid treatment conditions which are represented by points slightly below the 10 vol. percent curve when using 3 vol. percent of 86% acid. These are generally applicable successfully and give rise to no problems of sulphation, isomerisation or processing.

The criticality of the acid treatment of course, arises from the fact that sulphuric acid of strength sufficient to bring about a purification is strong enough to cause sulphation of the olefin itself. 86% sulphuric acid is a convenient acid for the treatment. It is strong enough to effect a purification yet not so reactive as to require a very short contact time.

The manner of mixing of the olefin and of the acid is relatively immaterial, provided that good contacting is obtained.

The product resulting from the acid treatment is a mix-

ture of two phases viz. a lower dark coloured acid layer, and an upper red olefin layer. When the acid treatment is carried out as recommended so that little or no sulphation as evidenced by the 8.4 micron absorbance ratio occurs, the mixture readily separates in the subsequent settling stage. If however, undue sulphation has been allowed to take place, the acid layer does not settle so readily and sulphation continues to occur in the settling stage. This causes difficulties in the acid removal step and eventual olefin spoilage. The two phases are separated as cleanly as possible, for example by centrifuging and the olefin layer is immediately treated with an adsorbent preferably in absence of atmospheric moisture. This olefin layer is neutral and requires no treatment prior to subjection to the adsorbent. The sludge layer can be recycled for acid treatment of fresh olefin. The two treatments i.e. acid followed by adsorbent can be carried out directly, i.e. sequentially without an intermediate step such as a washing step. Suitable adsorbents are fuller's earths, Celites (registered trademark) activated charcoal, clays or a clay-like material, aluminas, silicas, and aluminosilicates. The amount of adsorbent used is 1–15%, preferably 0.5–10% by weight of the olefin. The preferred adsorbent is an acid-activated fuller earth, for example that available as Type 237 from the Fuller's Earth Union Co. Ltd., Redhill, Surrey, with which the amount is preferably 1.3–6% by weight. This quantity is disproportionally less than is required with other fuller's earths, which are in turn, preferred to the remaining above-specified adsorbents. Silica gel, especially the chromatographic grade is also an efficient adsorbent, but has a far shorter life than has a fuller's earth as measured by the quantity of olefin it will treat. The amount of material requiring removal from the olefin layer is of course a factor in determining the amount of earth to be mixed with the olefin layer. Contact time is of the order of 5–10 minutes. The temperature at which the olefin layer and adsorbent are mixed is usually room temperature. Mixing is achieved by any of the usual methods, e.g. mere stirring together for example, for about 5 minutes, or percolation of olefin layer through the bed of adsorbent. The mixing need only be mild in nature.

The adsorbent removes the coloured compounds which stay dissolved in the olefin layer and which were formed by the previous treatment of the olefin with sulphuric acid; i.e. it removes the materials which harm the product sulphonate and which cannot be removed by purely physical methods by settling, centrifuging and which react with water to give coloured olefin soluble compounds. At the same time, the adsorbent removes traces of the highly coloured acid layer which may not have been removed in the preceding phase separation. The adsorbent treatment can be applied in one or more stages. The number of stages and the quantity of earth needed to obtain the required olefin quality depends on the quality of the starting olefins. The preferred amounts are $3\times1.3\%$ earth or $1\times6\%$. A one stage treatment has the obvious advantage of less handling and filtration. Where olefin is, because of inefficient mechanical separation, remaining on the earth, it can be recovered therefrom by simple boiling of the earth in water for a short time. Phase separation subsequently yields 75% olefin recovery. The residual earth maintains sufficient activity to be re-usable although possibly in greater quantity, for further olefin pre-treatment.

The adsorbents may be removed from the olefinic layer by filtration or sedimentation. Suitable methods are with filter presses, meta filters or solid bowl centrifuges. The separation will be found to be straightforward, when the process of the invention has been employed: If however, a process not according to the invention has been used, and particularly when sulphation has occurred, the resulting olefin is of poor quality and the adsorbent becomes sticky, extremely difficult to filter and forms a stable suspension.

The olefins resulting from the two stage treatment with sulphuric acid and fuller's earth have fewer colour forming impurities and are immediately suitable for sulphonation. Caustic and water washes are not necessary, neither is distillation required. The two stage treatment is effective to a surprising degree. Not only does it remove most of the colour forming impurities but it also removes some of the visible olefin colour.

Many of the sulphonates derived from olefins treated in this way are suitable for inclusion directly into detergent products. Others may require a bleaching treatment but in contrast to the sulphonates of the untreated olefins it is possible to bleach them to an acceptable colour level, i.e. the olefins pretreated according to the invention are much more amenable to bleaching treatment.

The process according to the invention may of course be applied on a continuous basis. The accompanying figure emphasises the need for short times of mixing the acid and olefins when acids of strength greater than 86% are used. When the treatment is required for quantities of olefin of up to 20 lbs. the control of mixing time presents no problem and the operation can be carried out batchwise. However, when large quantities of olefin are required, as for commercial use, batch operations are not feasible since the time taken to add the reagents to the mixing vessel can very often be greater than the maximum allowable mixing time. In large vessels it is virtually impossible to avoid mixing during the addition of the reagents. Continuous operation is thus to be preferred to enable control of mixing time.

The invention is also concerned with the additional step of preparing the sulphonate from the purified olefins. It is preferred to sulphonate using dilute SO_3 gas, e.g. SO_3/air using a film reactor, particularly a falling film reactor, having cooling water at about 20° C. The sulphonation conditions are selected from an olefin to SO_3 ratio, (expressed in moles) of from 1:0.7 to 1:2, preferably 1:1 to 1:1.5; a reaction temperature of 40–80° C., a residence time of olefin in contact with the SO_3/air stream of 0.5–30 seconds, preferably 5–20 seconds. The SO_3/inert gas stream is preferably SO_3/air in concentration SO_3:air of all SO_3 to 1:99, preferably 15:85 to 2:98. When sulphonation is carried out in a stirred tank reactor, then conditions are usually 20–45° C., 5–10% SO_3 vol. percent in air, 1.0:1 to 1.5:1 SO_3:olefin (in moles) and a reaction time of 10–50 minutes. There are other ways in which sulphonation of the purified olefins may be achieved, for example, reaction of atomised olefin with a diluted SO_3 stream.

The invention will now be described by way of examples. In these examples the product of sulphonation was collected and stirred with 5% aqueous sodium hydroxide for 2 hours at 95° C. The product was cooled and diluted with 50% isopropanol in water to give a solution containing 3.5% active detergent as measured by titration with cetyldimethylbenzylammonium choride. The solution colours were measured in a cell having a path length of 5¼" with a Lovibond tintometer. With this test, Lovibond values of 1.5–2, or less, red, and 7–9 or less yellow, are deemed to be of satisfactory colour level for inclusion of the product in coloured detergent compositions. For use in white powders or in white personal washing tablets, the requirements are far more stringent, and Lovibond colours of 0.7–0.9 red and 2.5–3.0 yellow are considered satisfactory. In many of the examples, the improvement in colour of the sulphonate resulting from the process is sufficient for direct inclusion of the product into detergent compositions. In other examples, althrough the colour of the sulphonate has been improved substantially, bleaching is required to bring the colour levels to the desired standard.

EXAMPLE 1

Olefins derived from a wax cracking process and which were predominantly C_{15}–C_{20} alpha-olefins were fed directly to a falling film sulphonator reactor 0.81" internal diameter, 8' in height, at a rate of 20 lbs./hour together with SO_3 (8.3 lbs./hour) admixed with dry air, the SO_3

concentration being 4 vol. percent. The residence time was 10 secs. The results were as follows:

Olefin Feed	Pre-treatment	Sulphonation Conditions: Moles SO_3 per mole olefin	Sulphonation Conditions: Temp., ° C.	Sulphonate Colour Lovibond: Red	Sulphonate Colour Lovibond: Yellow
C_{15}-C_{20} cracked wax olefins	None	1.0	51	3.0	18
		1.25	58	4.2	40

EXAMPLE 2

3 litres of the olefins as used in Example 1 were subjected to pretreatment according to the invention. They were shaken with 150 mls. of 86% H_2SO_4 for 10 minutes at 25%. The mixture was allowed to settle for 10 minutes and then phase-separated. The upper layer was mixed with 90 g. of acid-activated fuller's earth, and filtered. The fuller's earth treatment was repeated and gave a bright, clear olefin layer, which amounted to 97% of the starting material. Olefin isomerisation could not be detected from the infrared spectrum by reference to the trans band at 10.4 mμ. The pretreated olefins were then fed to the sulphonation reactor as described in Example 1. The results were as follows, and show the greatly improved colour properties of the sulphonates of Example 2 over those of Example 1.

Pretreatment	Sulphonation Conditions: Moles SO_3 per mole olefin	Sulphonation Conditions: Temp., ° C.	Sulphonate Colour Lovibond: Red	Sulphonate Colour Lovibond: Yellow
Sulphuric acid 86% 1 x 5 vol. percent followed by 2 x 3 wt. percent Fuller's earth.	1.0	52	1.6	5.0
	1.3	57	1.5	7.0

EXAMPLE 3

An experiment, similar to that of Example 2, wherein the same acid treatment was used, repeated 3 times and was followed by a caustic wash and a water wash as proposed in the literature gave the following results:

Sulphonation Conditions: Moles SO_3 per mole olefin	Sulphonation Conditions: Temp., ° C.	Sulphonate Colour Lovibond: Red	Sulphonate Colour Lovibond: Yellow
1.0	52	1.3	7.0
1.25	56	1.4	9.0

Although these sulphonates are of good colour, this process is difficult and relatively expensive by virtue of the many steps involved as discussed above. Here, olefin recovery following the combined acid, caustic and water treatment was only 88%, in contrast to the 97% recovery from the process according to the invention used in Example 2.

EXAMPLE 4

An experiment in which a 4% fuller's earth treatment was applied to the olefins, without the acid treatment gave the following results, on sulphonation according to Example 1.

Sulphonation Conditions: Moles SO_3 per mole olefin	Sulphonation Conditions: Temp., ° C.	Sulphonate Colour Lovibond: Red	Sulphonate Colour Lovibond: Yellow
1.0	48	2.1	11.0
1.25	55	2.1	11.0

EXAMPLE 5

An experiment in which a 25% activated silica gel treatment was applied to the olefin again without acid treatment gave the following results on sulphonation according to Example 1.

	SO_3/olefin	Red	Yellow
Untreated C_{15}-C_{20} olefins	1.25	6	40
SiO_2 treated [1] 4 lbs. of olefin per lb. SiO_2	1.25	5	12

[1] BDH "chromatographic Grade".

Thus the combined sulphuric acid-fuller's earth treatment is superior to treatments with the individual agents by themselves and indeed superior to treatment with much larger quantities of a far more powerful adsorbent by itself. Poor olefin recoveries result from the sulphuric acid treatment, while fuller's earth alone did not give sulphonates of acceptable colour.

EXAMPLES 6–9

The efficiency of the process according to the invention is further demonstrated by the following typical examples.

EXAMPLE 6

C_{15-20} cracked wax alpha-olefins light yellow-green in colour were treated with 5 vol. percent H_2SO_4 (86%) and stirred for ¼ hour. After settling for ¼ hour the acid was run off and the olefin layer was treated with 3×1.3% earth (Type 237) with filtration between each earth treatment. Sulphonation using an 8′ x 0.81″ internal diameter falling film reactor at 20 lbs. olefin throughput/hour with a cooling water temperature around 21° C. was used. The residence time is approximately 10 seconds. The results are as follows:

	SO_3 alpha olefin	Percent conversion	Lovibond: Red	Lovibond: Yellow
Untreated	1.00	67	3.0	18.0
Treated	1.00	65.6	0.7	1.7
Untreated	1.25	87	4.2	40.0
Treated	1.25	73.3	0.7	1.9
Untreated	1.5	90.8	4.7	28.0
Treated	1.5	86.8	1.2	6.0

EXAMPLE 7

Using the process as described in Example 6 but with increase of the throughput to 25 lbs. olefin per hour, the results were as follows:

	SO_3 alpha olefin	Percent conversion	Lovibond: Red	Lovibond: Yellow
Untreated	1.0	67.1	3.0	17.0
Treated	1.0	71	1.5	6.0
Untreated	1.25	84.8	4.0	17.0
Treated	1.25	84.3	1.8	7.4

EXAMPLE 8

Using the process as described in Example 6, but with

decrease of throughput to 15 lbs. per hour, the results were as follows:

	SO_3 alpha olefin	Percent conversion	Lovibond Red	Lovibond Yellow
Untreated	1.0	64	2.6	13.0
Treated	1.0	60.8	1.6	7.0
Untreated	1.25	80.4	3.0	14.1
Treated	1.25	78.8	1.4	5.2
Untreated	1.4	87.5	3.1	19.0
Treated	1.4	86.0	2.1	10.0
Untreated	1.5	91.3	4.3	43.0
Treated	1.5	90.5	2.4	15.0

now free of red colour, clear and non-acidic was sulphonated as described in Example 6. Where the olefin leaving the settler contained an undesirably large quantity of suspended acid sludge this was removed by passing through a pad of glass wool to coalesce the acid.

The purified olefin was then sulphonated in the reactor described in Example 1, under the listed SO_3 concentrations and conversions. It will be noted that very high conversions (i.e. percent olefin reacted) were successfully used. The Lovibond values are again for the unbleached sodium sulphonate.

CONTINUOUS ACID TREATING OF C_{15}–C_{18} CHEVRON ALPHA-OLEFINS

	Acid treatment/Earth treatment						1.4 moles SO_3			1.25 moles SO_3		
Run	Acid Strength, Wt., Percent	Acid Vol., Percent	Res. Time Reactor, minutes	Res. Time Settler, minutes	8.4:6.25 Micron Absorbance Ratio	10.4:10.1 Micron Absorbance Ratio	Conversion, Percent	Sulphonate Colour (Lovibond) Red	Sulphonate Colour (Lovibond) Yellow	Conversion, Percent	Sulphonate Colour (Lovibond) Red	Sulphonate Colour (Lovibond) Yellow
10	86	3.0	10	41	0.11	0.02	99.2	3.4	12.7	93.5	2.1	10.5
11	86	3.0	2	8.5	0.00	0.02	99.0	3.9	13.7	93.5	3.6	13.2
12	90	0.5	1.2	2.2	0.00	0.02	99.6	2.1	9.1	9.57	3.5	14.1
13	90	0.5	1.2	2.2	0.00	0.02	500	8.4	18.6	97.9	3.2	12.3
14	86	3.0	2.1	6.6			99.3	2.8	11.4		1.4	8.1
15	85	3.0	2.1	6.6			99.4	3.5	13.2	94.2	2.0	12.0
16	84	3.0	2.1	6.6			100	3.2	12.1	94.1	1.6	23.4
17	86	3.0	2.1	6.0	0.0	0.02	100	4.1	23.0	94.5	1.6	9.9
Control	None				0.00	0.02	98.0	5.4	25.7	89.7	6.6	23.4

EXAMPLE 9

C_{15-18} cracked wax olefins were treated with 3 vol. percent H_2SO_4 (86%) and stirred for 3–5 mins. After 10 mins. settlement the olefin layer was treated with 1× 6% (Type 237 fuller's earth) and sulphonated under the conditions of Example 6.

	SO_3 alpha olefin	Percent conversion	Lovibond Red	Lovibond Yellow
Untreated	1.0	65.5	6.1	45.0
Treated	1.0	67	1.6	7.1
Untreated	1.4	65.8	6.2	40.0
Treated	1.4	93.5	2.5	12.0

The following notes refer to the foregoing Examples 6–9.

(1) Lovibond values are for the unbleached sodium sulphonate.

(2) Conversion is percent olefin reacted.

The foregoing Examples 6–9 clearly demonstrate the improvement in sulphonate colour which is achieved by the pretreatment of the olefin according to the invention. The quantity of the improvement decreases with the increasing conversion but the improvement is present to a significant degree over the whole range of conversions quoted above.

EXAMPLES 10–17

The following table gives the results of experiments on the application of the invention to continuous operation. In these, the olefins and sulphuric acid were pumped separately to a small stirred tank reactor using the conditions specified in the table below. The mixture was allowed to overflow to a settling vessel where phase separation of the acid and olefin layer took place. The acid was run off from the bottom of the settler and the olefin was treated semi-continuously with fuller's earth Type 237. This operation was carried out by allowing the olefin to overflow from the settler to a stirred tank containing a prescribed quantity of the earth. When sufficient olefin had been added to provide a 6% concentration of earth, the olefin from the settler was passed to a second earth treating tank. The earth was removed from the olefin-earth slurry using a metafilter and the olefin which was

The olefins from these acid treatments/earth treatments contain little or no di-alkyl sulphate and no more internal olefin than was in the olefin before treatment, as judged by infra-red analysis. The foregoing results clearly demonstrate the improvement in sulphonate colour obtained by the pretreatment of the olefins according to the invention. It will be understood that although some of the colour levels of the treated olefins lie outside the limits expressed as suitable for detergent products, the sulphonates of the treated olefins may be bleached readily, so as to bring the colour levels within the specified range.

EXAMPLE 18

The improved bleachability of sulphonates of pretreated olefins will now be illustrated by way of Example 18. This shows that the sulphonates from pretreated olefins can be bleached to a lighter colour than can the sulphonates of the untreated olefin, and that less bleaching agent is required for this operation. A 30% active detergent slurry of the neutralised and hydrolysed sulphonate product obtained as described above, was heated on a steam bath to 70° C. and sodium hypochlorite bleach added in sufficient quantity to provide a concentration listed in the table below. The temperature was maintained for 30 minutes and then the mixture allowed to cool before measuring the colour.

	Before Bleaching Red	Before Bleaching Yellow	Percent bleach [1]	After Bleaching Red	After Bleaching Yellow
Untreated	4.7	28	1	1.3	5
			2	1.2	4
			3	1.0	3.8
Treated—3 vol. percent 86% H^2SO_4. 15 mins., 3 x 1.3 wt. percent type 237 Fuller's Earth.	2.5	13	1	0.9	2.4
			2	0.9	2.1
			3	0.9	1.6

[1] Measured as wt. of available chlorine per 100 wt. units of active detergent, the active detergent being measured by titration with cetyldimethylbenzylammonium chloride.

Whilst the process has been described with respect to alpha-olefins, it is applicable to random olefins, although in the latter case, the sulphuric acid treatment is less critical, there being no real problem of isomerisation. When the process of the invention is applied to random olefins, the sulphonates derived therefrom have appreciably improved colour over sulphonates prepared from either direct sulphonation of random olefins, with subse-

quent bleaching, or sulphonation of random olefins, which have been treated with acid followed by caustic and water washing and distillation.

We claim:

1. In a process for the manufacture of alpha-olefin sulphonates, the improvement yielding an alpha-olefin sulphonate with acceptable color for use in a detergent composition which comprises treating an alpha-olefin with from about 2% to about 7% by volume of sulfuric acid having an acid strength of about 85% to about 87% by weight of sulfuric acid for about 2 to about 10 minutes so as to avoid sulphation and isomerization of said olefins, and to provide an olefin layer and an acid layer, phase separating said olefin layer, treating said olefin layer with an acid-activated fuller's earth, separating the purified olefin layer therefrom, and subjecting the resulting olefin to sulphonation and neutralization/hydrolysis.

2. A process according to claim 1 wherein said acid contacting conditions are 85–87% acid strength (by weight H_2SO_4), 2–7 vol. percent H_2SO_4 and 2–10 minutes.

3. A process according to claim 1 wherein said adsorbent is selected from an earth, a clay, activated charcoal and a silicate.

4. A process according to claim 1 in which said earth is present in amount 1–15% by weight of said olefin layer.

5. A process according to claim 1 in which said olefin layer is treated with said earth in absence of atmospheric moisture.

6. A process according to claim 1 which includes an additional step of treating said purified olefin layer with at least one treatment with said earth.

7. In a process for the manufacture of alpha-olefin sulphonates in which an alpha-olefin is reacted with a sulphonating agent, the improvement yielding an alpha-olefin sulphonate with acceptable color for use in a detergent composition which comprises the steps of:

(i) contacting with said olefins from about .1% to about 50% by volume of aqueous sulfuric acid having a concentration of about 70% to about 98%, for a period of about .1 to about 60 minutes

(ii) allowing said olefin and sulfuric acid mixture to separate into an acid layer and an olefin layer

(iii) treating said olefin layer with an absorbent, and

(iv) separating said absorbent from said olefin

(v) said sulfuric acid concentration, volume percent and contact time with the olefin being such that the ratio of absorbence of an infra-red spectrum of the resulting olefin at 8.4μ to that at 6.25μ is no greater than .25 and at 10.4μ to 10.1μ is no greater than that of the starting olefin.

8. The process of claim 7 wherein the resulting olefin is subjected to sulphonation and neutralization/hydrolysis.

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U.S. Cl. X.R.

260—677

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,492,343 Dated April 20, 1967

Inventor(s) Philip James Garner and Howard Neilson Moulden

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 32 change "absorbent" to --adsorbent--.

Column 3, line 56 change "80-90Z" to --80-90%-- and change "86Z" to --86%--.

Column 5, line 68 change " : " to -- . --.

Column 7, line 18, Example 2 change "25%" to --25°C--.

In the Table entitled "Continuous Acid Treating of C_{15}-C_{18} Chevron Alpha-Olefins":

Under heading "1.4 moles SO_3 - Conversion, Percent" for Run 13 change "500" to --100--.

Under heading "1.25 moles SO_3 - Conversion Percent" for Run 12 change "9.57" to --95.7--.

Under heading "1.25 moles SO_3 - Sulphonate Colour (Lovibond) Yellow" for Run 16 change "23.4" to --9.4--.

In the Claims:

Claim 2, line 1 change "Claim 1" to --Claim 7--.

Claim 3, line 1 change "Claim 1" to --Claim 7--.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

SIGNED AND SEALED
AUG 18 1970

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents