This invention relates to a process for the production of alpha-naphthol (1-naphthol), and more particularly to a process which includes sulfonating naphthalene to form 1-naphthalene-monosulfonic acid, and fusing the monosulfonic acid with caustic alkali.

Alpha-naphthol (1-naphthol), which finds extensive use as an intermediate product in the manufacture of various synthetic products, such as dyes is frequently employed in processes in which the presence of 2-naphthol is undesirable and sometimes harmful. It has been the general practice heretofore to prepare 1-naphthol substantially free from 2-naphthol by hydrolyzing 1-naphthylamine with dilute sulfuric acid under pressure. This process is expensive however owing to the high cost of the 1-naphthylamine and the high cost of equipment and maintenance thereof.

An object of the invention is to produce 1-naphthol substantially free from 2-naphthol by a process which includes the sulfonation of naphthalene to form 1-naphthalene-monosulfonic acid and the subsequent fusion of the sulfonic acid with caustic alkali and which process gives an improved quality of 1-naphthol directly from naphthalene economically and readily on a commercial scale.

An additional object of the invention is to sulfonate naphthalene under such conditions that there is formed a mixture which contains 1-naphthalene-monosulfonic acid and a naphthalenedisulfonic acid and which is substantially free from 2-naphthalene-monosulfonic acid, and recover 1-naphthalene-monosulfonic acid in a relatively purified condition from the resulting reaction mass.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to others thereof which will be exemplified in the process hereinafter disclosed. The scope of the invention will be indicated in the claims.

In the practice of the present invention naphthalene is sulfonated under such conditions that there is formed a reaction mass containing 1-naphthalene monosulfonic acid and sulfuric acid but containing less than 2 per cent. of 2-naphthalene-monosulfonic acid and preferably substantially free from 2-naphthalene-monosulfonic acid, and the resulting 1-naphthalene-monosulfonic acid is separated from the reaction mass.

The 1-naphthalene-monosulfonic acid is then converted to 1-naphthol, as by fusing the resulting 1-naphthalene-monosulfonic acid with caustic alkali to form the alkali-metal compound of 1-naphthol, and liberating the 1-naphthol from the alkali-metal compound.

The sulfonation may be carried out by adding naphthalene to well-stirred concentrated sulfuric acid while maintaining the temperature at about 15° to 30° C., preferably at 20° to 25° C., and the sulfonation is allowed to continue at said temperature after the addition of the naphthalene is complete. The naphthalene is preferably in finely divided form, and may be added in portions and at such a rate that cooling to the desired extent may be readily accomplished without danger of local overheating.

Sulfuric acid of a strength ranging from about 93 to 100 per cent. may be employed, the stronger acid being preferred inasmuch as its use leads to a less amount of unsulfonated naphthalene in the product. The acid is preferably employed in the proportion of about three to about four parts by weight of acid per part by weight of naphthalene, but other amounts of acid may be used.

If too little acid is used, however, stirring of the mass becomes extremely difficult and desulfonation may result.

For the preparation of a 1-naphthol substantially free from 2-naphthol, it is essential that the sulfonation be conducted in such a manner that very little, if any, 2-naphthalene-monosulfonic acid is obtained. I have found that if the 1-naphthalene-monosulfonic acid is caused to crystallize substantially as soon as the reaction mixture becomes supersaturated with respect to it, or as soon thereafter as is possible, and crystallization is caused gradually to continue throughout the sulfonation, less than 2 per cent., and usually substantially no 2-naphthalene-monosulfonic acid is obtained, but 1,5- and 1,6-naphthalenedisulfonic acids are obtained. If, however, the reaction mixture does not crystallize, a considerable amount of 2-naphthalene-monosulfonic acid is produced, or if the reaction mixture is permitted to become excessively supersaturated with respect to 1-naphthalene-monosulfonic acid, sudden spontaneous crystallization of the whole reaction mixture may result, accompanied by excessive liberation of heat together with setting of the mixture to a solid mass which no longer can be stirred, and also leading to the production of a considerable amount of 2-naphthalene-monosulfonic acid.

Under the conditions of the present process, the reaction mixture will have become super-
saturated with respect to the 1-naphthalene-
monosulfonic acid within a short period of the
time when all of the naphthalene has been added.
It sometimes happens that the mass seeds itself
and the 1-naphthalene monosulfonic acid gradu-
ally precipitates as it is produced. In order to
insure the desired crystallization, the reaction
mixture is seeded substantially as soon as it be-
comes saturated with respect to the 1-naphtha-
lenemonosulfonic acid, and if this does not cause
crystallization, seeding is repeated at short in-
tervals until the 1-naphthalenemonosulfonic acid
begins to crystallize out of solution. In seeding
the reaction mixture, there may be used either
a crystal, or crystals, of 1-naphthalenemonosul-
fonic acid or of a soluble salt of said sulfuric
acid. I have found that 1-naphthalenemonosul-
fonic acid can be crystallized from a super-
saturated solution of the same by the addition
of a supersaturated solution of a crystal of a
soluble salt of said acid. Obviously, instead of
seeding to induce crystallization of the 1-naph-
thalenemonosulfonic acid, the apparatus in con-
tact with the sulfonation reaction mixture as if
example, the agitator employed for stirring the
reaction mixture, may be rubbed or scratched to
induce the crystallization.
To complete the sulfonation, the reaction mix-
ture is maintained at the reaction temperature
(15° to 30° C., preferably 20° to 25° C.) for a
period of from about 2 or 3 to about 40 hours
after completion of the addition of the naphtha-
lene. The total reaction time will depend upon
the specific conditions employed, such as the
amount and strength of sulfuric acid. A satis-
factory combination of reaction conditions is set
forth in the example hereinafter given.
It is noted that the crystallization of the 1-
naphthalenemonosulfonic acid removes water
from the reaction mixture and thus assists in
reducing the amount of 2-naphthalenemonosul-
fonic acid obtained. Inasmuch as 1-naphtha-
lenemonosulfonic acid crystallizes with two mole-
cules of water, its crystallization strengthens the
sulfuric acid in the reaction mixture, and by con-
tinuing the sulfonation in the presence of the
strengthened sulfuric acid, the 2-naphthalene-
monosulfonic acid is further sulfonated to disul-
fonic acids.
As a result of the sulfonation there is obtained
a magma which comprises 1-naphthalenemono-
sulfonic acid suspended in the spent sulfuric acid
which holds in solution the largest portion of the
by-products of the sulfonation. These impurities
consist chiefly of naphthalenedisulfonic acids,
of other matter derived from the naphthalene
and sulfuric acid charged to the process, and
small amounts of mineral salts.
After the completion of the sulfonation, the
1-naphthalenemonosulfonic acid is separated
from the remaining reaction mixture. I have
found, inasmuch as at the end of the sulfonation
step the largest portion of impurities and by-
products of the sulfonation, including those re-
sulting from small amounts of impurities in raw
materials used, which those which enter through
the composition of sulfonation apparatus, are in solu-
while the desirable product (1-naphthalene-
monosulfonic acid) is in the form of crystals sus-
pended in the acid solution, that by subjecting
the magma to filtration or other procedure for
separation of the crystals from the liquid, the
crystals of 1-naphthalenemonosulfonic acid are
obtained substantially free from the impurities,
which are held in solution. The cake can be
purified further by washing rapidly with small
portions of sulfuric acid to displace retained
liquor. The filtrate resulting from these washes
may be collected separately and used as part of
the sulfuric acid charge feed of another sulfonat-
ion. The separation may be effected in any suitable
manner; e.g., by filtration on a vacuum or other
filter adapted for filtering slurries which contain
highly corrosive acid substances. Such a filter
may consist of a lead-lined iron tank with a flat 10
bottom, connected through a bottom outlet, to a
receiver which is suitably fabricated to receive
and hold sulfuric acid of varying strengths. A
grid which consists of bars of lead or other suit-
able material and rests on the flat bottom of the
tank, supporting a plate or plates which are fab-
ricated from or are covered with a suitable
material, for example, alumnum, Monel metal or
asbestos cloth, etc., may be employed to form
the filtering medium. Vacuum is applied to the
underside of the filtering medium, the filtrate is
drawn through the filtering medium and flows
through ports in the sides of the grid, and by
way of the outlet of the tank, to the receiver pro-
vided for the purpose.
The resulting separated 1-naphthalenemono-
sulfonic acid is converted to the alkali metal salt
for use in the fusion operation in any suitable
manner. Thus the washed or unwashed filter-
cake of 1-naphthalenemonosulfonic acid may be 30
1 dissolved, suspended or slurred in as much or
little water as is found convenient or desirable,
and then converted to the sodium or potassium
salt, for example, by neutralising an aqueous
solution of the 1-naphthalenemonosulfonic acid
at 25
while hot with sodium or potassium sulphite, the
sulfur dioxide formed being removed by boiling,
adding a sodium or potassium salt to the hot
solution to salt out the sodium or potassium salt
of the 1-naphthalenemonosulfonic acid, cooling
30
the resulting solution and separating the 1-naph-
thalenemonosulfonic acid salt; or by treating an
aqueous solution of the 1-naphthalenemonosul-
fonic acid with a suitable calcium compound (e.
g. calcium carbonate, calcium sulphate, calcium 40
oxide, calcium hydroxide, etc.) so as to convert
the 1-naphthalenemonosulfonic acid and any
excess sulfuric acid present to their calcium salts,
filtering off insoluble calcium sulphate which may
be present, converting the calcium 1-naphtha-
lemonosulfonate to an alkali metal sulfonate
by the addition of a suitable alkali metal com-
pound (e.g. sodium carbonate, potassium car-
bonate, sodium sulfite, potassium sulfite, etc.),
filtering off the insoluble calcium salt formed, 5\text{5}
and crystallizing the alkali metal salt of 1-naph-
thalenemonosulfonic acid from the resulting
filtrate, preferably with the aid of evaporation
or the further addition of a suitable alkali metal
salt such as sodium or potassium chloride; or by 60
treating an aqueous solution of the 1-naphtha-
lenemonosulfonic acid, preferably while hot, with
sodium or potassium chloride or other suitable
salt to convert it to the sodium or potassium
salt, and recovering the sodium or potassium salt 65
of the 1-naphthalenemonosulfonic acid, preferably
by cooling and filtering; etc.
In carrying out the fusion in accordance with
a preferred method of procedure, the 1-naphtha-
lenemonosulfonic acid salt obtained as above de-
scribed is fused under pressure in a steel melt-
in with an excess of caustic alkali under such con-
ditions that the 1-naphthalenemonosulfonic acid
is converted to an alkali-metal 1-naphtholate.
The caustic alkali (e.g., sodium hydroxide, po-
tassium hydroxide, or a mixture thereof) is preferably employed in such proportions relative to the 1-naphthalenemonsulfonic acid that there is present in the melt at least sufficient excess caustic alkali to form a flux and render the melt capable of being agitated at the reaction temperature. The fusion may be carried out at a temperature of about 275° C. to 310° C., preferably at a temperature not exceeding 285° C., and preferably for a minimum reaction period of about 5 1/2 to 6 hours at the reaction temperature. Upon completion of the fusion, the 1-naphthol may be isolated from the fusion mixture, e. g. by extracting the fusion mass from the alkali metal 1-naphthalenolate or alkali metal 1-naphthalene-8-sulfonate with 20% potassium hydroxide or a mixture thereof in the form of flakes or chips. As an illustrative embodiment of a manner in which the invention may be practiced, the following example is presented.

**Example**

**Sulfonation of naphthalene.**—500 pounds of ground naphthalene is charged in portions and with good agitation to a sulfonating kettle which contains about 2000 pounds of sulfuric acid (100%). The rate of charging of the naphthalene is such that it requires approximately 3 hours for the addition of the whole charge. The temperature of the sulfonation mass is kept throughout the charging operation at a temperature of about 20° to about 25° C. In order to prevent, so far as possible, the formation of 2-naphthalenemonsulfonic acid, the 1-naphthalenemonsulfonic acid is caused to crystallize as early in the sulfonation as possible; for, the earlier the crystallization of the 1-naphthalenemonsulfonic acid occurs, the smaller is the quantity of 2-naphthalenemonsulfonic acid produced. If crystallization should not have commenced before all of the naphthalene has been added, when addition of naphthalene is complete, the reaction mixture is seeded at intervals with small portions of crystals of 1-naphthalenemonsulfonic acid until crystallization has been induced. After all of the naphthalene has been added, the reaction is allowed to continue for an additional period of about 10 hours while still maintaining the temperature at about 20° to about 25° C.

After completion of the sulfonation (total time about 13 hours from the start of charging the naphthalene), the sulfonation reaction mass which is in the form of a magma of the 1-naphthalenemonsulfonic acid crystals in admixture with a sulfuric acid solution of about 83 to 85 per cent strength, containing naphthalenedisulfonic acids and other impurities dissolved therein, is filtered, preferably on a vacuum filter. The resulting filter cake is dissolved in about 3000 pounds of water and the resulting mass, while hot, is treated with sufficient sodium sulfite to render the mixture neutral to Congo red paper. The mixture is boiled to drive off sulfur dioxide and then sodium chloride is added to the hot mixture until the density of the resulting solution is about 18° to 20° Bé. The resulting mass is then cooled, for example, to 25° C., and the precipitated sodium salt of 1-naphthalenemonsulfonic acid is recovered by filtration. The resulting filter cake, which contains about 50 per cent of water and about 45 to 48 per cent of 1-naphthalenemonsulfonic acid sodium salt and which is practically free from 2-naphthalenemonsulfonic acid and its sodium salt, may be dried, for example, in an atmospheric drier at a temperature of about 110° C. In the manufacture of alphaphthalon by caustic alkali fusion, however, it is not necessary to dry the filter cake.

**Alkali fusion of the sulfonic acid mixture.**—250 pounds of the filter cake obtained in the above described manner, and comprising the sodium salt of 1-naphthalenemonsulfonic acid, is mixed with about 205 pounds of solid sodium hydroxide (98%), and the mixture is added to an autoclave equipped with an agitator. The autoclave is closed, and the mixture is gradually heated to a reaction temperature of about 280° to 285° C. and is maintained at said reaction temperature until the reaction is complete, which usually requires about 6 hours. Agitation is begun as soon as the mass becomes sufficiently pasty to be stirred. Upon completion of the fusion, the autoclave is cooled to reduce the pressure, hot water is pumped in under pressure, and, after further cooling, the autoclave is opened and additional water is added to complete the solution of the melt. The solution is then filtered to remove solid impurities, the filtrate is heated to a temperature above the melting point of 1-naphthol (e. g., to about 75° C.) and dilute sulfuric acid (50° Bé.) is added until the alkalinity of the solution toward phenolphthalein paper just disappears (about 290 to 310 pounds being required). The 1-naphthol is thereby precipitated in the form of 35% oily globules. The mass is cooled to a temperature below the setting point of 1-naphthol (e. g., to about 35° C.) to solidify and complete the precipitation of the 1-naphthol, which is then separated by filtration. The filter cake is washed with water until a test with brilliant yellow paper shows no alkaline reaction, and it is then blown for a short time with air.

The 1-naphthol obtained as a result of the above process is substantially free from 2-naphthol, from naphthalene sulfonic acids, and from naphthalenedisulfonic acids; and it is of sufficient purity for employment in the manufacture of dyestuffs, e. g., Orange I (C. I. No. 150), without further treatment. If desired, it may be further purified by vacuum distillation, and the distillate may be flaked.

It will be realized that the invention is not limited to the process and the details thereof which are set forth in the foregoing example. Thus, the sulfonation may be carried out with a sulfuric acid of a strength lower than 100 per cent., e. g., 95 per cent. sulfuric acid, but when such weak sulfuric acid is employed a part of the naphthalene is not sulfonated, and it is more difficult to induce crystallization. The amount of sulfuric acid employed may be varied, but an amount is preferably employed such that the sulfonation mass can be readily stirred throughout the sulfonation. The rate at which the naphthalene is incorporated with the sulfuric acid may be varied, but for optimum results it is desirable that the addition should not take place so rapidly that local overheating occurs or that the temperature of the mass exceeds about 30° C. It may not always be necessary to seed the sulfonation mass in order to induce a gradual crystallization of the 1-naphthalenemonsulfonic acid; but unless crystallization of the 1-naphthalenemonsulfonic acid is caused to occur at
an early stage in the sulfonation, and preferably as soon as the reaction mixture has become supersaturated with respect to 1-naphthalene-
omonsulfonic acid, 2-naphthalenemonosulfonic acid will be produced. Furthermore, crystallization may otherwise suddenly occur at a later stage in the sulfonation, causing the mixture to tend to a solid mass which can no longer be agitated, and liberating a considerable amount of heat, thereby undesirably raising the temperature of the sulfonation mass. A total reaction time of about 10 to 15 hours is recommended for maximum yields of 1-naphthalene-
omonsulfonic acid, but if desired, and if the accompanying loss in yield of 1-naphthalene-
omonsulfonic acid is not of consequence, the sulfonation may be terminated about 2 or 3 hours after all of the naphthalene has been added to the reaction mixture.

The separation (e.g., filtration) of the 1-naphthalenemonosulfonic acid from the sulfonated reaction mass is preferably carried out with a mixture in which the total acidity of the magma calculated as sulfuric acid, is not less than about 25 to 30 per cent. If the acidity should be less than this value, the mass is preferably fortified with stronger sulfuric acid prior to the separation. Further, the separation (filtration) is preferably carried out at a temperature of about 20°C to about 25°C.

The press cake containing the sodium salt of 1-naphthalenemonosulfonic acid need not be dried for use in the subsequent alkali fusion process, and is advantageously used in the moist condition; inasmuch as the presence of the moisture enables the fusion to be carried out at the lower temperatures, and leads to a purer product and a somewhat higher yield. In carrying out the fusion of the sulfonic acids, temperatures of about 275°C to 310°C may be employed, the lower temperatures being preferred to the higher temperatures. For optimum results, the fusion is conducted at the lowest temperature at which the mass may be well stirred.

The period of heating at the reaction temperature may also be varied, but a period of about 5½ to 6 hours at a reaction temperature of about 260°C to 265°C leads to a maximum yield of 1-naphthol. At a lower temperature a somewhat longer time is required.

Sodium or potassium hydroxide or a mixture thereof may be employed in the fusion; and the proportion thereof employed relative to the naphthalene sulfonic acid mixture may be varied. The use of too little caustic, however, will lead to difficulty in agitating the melt.

The free 1-naphthalenemonosulfonic acid may also be subjected to the fusion operation without intermediate conversion to the alkali-
metal salt; but in that case sufficient additional caustic alkali is employed in the fusion to convert the free acid to the alkali-metal salt.

The fusion is preferably conducted with the exclusion of air; for, the presence of air in caustic alkali fusions of the type of the present process leads to some decomposition and contamination of the product.

Isolation of 1-naphthol and separation of it from the naphthalene sulfonic acids present in the melt in the form of their sodium salts may be effected by the addition of sulfuric acid of any suitable strength, and instead of sulfuric acid, other acids, e.g., hydrochloric acid, may be used. The use of too strong sulfuric acid (e.g., 100%) should be avoided, however, since local sulfonation of the product and consequent loss of yield may result during acidification under the temperature conditions employed. The amount of acid used may be varied, but an amount is preferably used such that the hydrogen ion concentration of the resulting solution expressed in terms of pH lies within the range of about 8 to about 9 inclusive. Under such conditions of acid concentration, substantially all of the sodium naphthalate is converted to naphthol while the sodium sulfite is substantially unaffected and is left in solution. This condition is indicated by the solution's ceasing to react alkaline toward phenolphthalein paper while it still reacts strongly alkaline toward brilliant yellow paper. A greater acidity (i.e., lower pH value) than about that given above may lead to the formation of bisulfite and loss in yield of naphthol, due to formation of a soluble naphthol sulfite ester.

The temperature of precipitation of the 1-
naphtol may be other than that specifically mentioned, but by effecting the precipitation at an elevated temperature, the liquid phase is caused to separate as oily globules, which on subsequent cooling congeal, with a minimum of occlusion, to readily filterable pellets. In cooling the precipitated 1-naphthol, care should be taken to avoid excessive cooling if sulfuric acid has been employed to liberate the naphthol from the sodium naphthalate, otherwise Glauber's salt may separate and contaminate the product.

The invention thus affords an improved method of producing 1-naphthol substantially free from 2-naphthol by a process which includes the sulfonation of naphthalene to form 1-naphthalene-
omonsulfonic acid and the subsequent fusion of the sulfonic acid with caustic alkali. It permits, in the sulfonation of naphthalene with sulfuric acid, of the production of 1-naphthalene-
omonsulfonic acid substantially free from 2-
naphthalenemonosulfonic acid, and of the production of a good quality of 1-naphthalenemono-
sulfonic acid from a mixture which contains 1-naphthalenemonosulfonic acid, a naphthalene-
diisulfonic acid but less than 2 per cent and even substantially no 2-naphthalenemonosulfonic acid. It further makes it possible to produce 100 percent purified 1-naphthalenemonosulfonic acid at low cost in commercial quantities. Such material is especially desirable for the production of alpha-
naphthol by the fusion process. Alpha-naphthol produced from the said material is substantially free from beta-naphthol, dihydroxy naphthalene, etc., which are the objectionable impurities commonly found in alpha-naphthol made by the usual caustic alkali fusion of commercial grades of 1-
naphthalenemonosulfonic acid available to the art prior to my invention.

The process of the present invention offers a further advantage in that it permits the utilization for the purposes of manufacture of 1-naphthalenemonosulfonic acid, of a lower grade of naphthalene than has been used or considered desirable heretofore, since the impurities thus introduced are eliminated by the purification step of this invention.

Since changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustration and not in a limiting sense, except as limited by the claims.

This application is a continuation-in-part of...
my Patent No. 1,962,137 of June 12, 1934, for "Production of alpha-naphthol". I claim:

1. A process for the production of 1-naphthol which comprises sulfonating naphthalene under such conditions that there is produced a reaction mass containing crystallized 1-naphthalenemonosulfonic acid and sulfuric acid but containing less than 2 per cent of 2-naphthalenemonosulfonic acid, separating the crystallized 1-naphthalenemonosulfonic acid from the remaining reaction mass, and fusing said 1-naphthalenemonosulfonic acid with a caustic alkali.

2. A process for the production of 1-naphthol which comprises sulfonating naphthalene under such conditions that there is produced a mixture containing crystallized 1-naphthalenemonosulfonic acid in admixture with a solution of 2-naphthalenemonosulfonic acid in sulfuric acid, which mixture is substantially free from 2-naphthalenemonosulfonic acid, separating the crystallized 1-naphthalenemonosulfonic acid from the remaining solution, and fusing said 1-naphthalenemonosulfonic acid with a caustic alkali.

3. A process for the production of 1-naphthol which comprises sulfonating naphthalene under such conditions that there is produced a mixture containing crystallized 1-naphthalenemonosulfonic acid in admixture with a solution of a naphthalenedisulfonic acid in sulfuric acid, which mixture is substantially free from 2-naphthalenemonosulfonic acid, controlling the acidity of the mixture so that the total acidity, calculated as sulfuric acid, is at least 50 per cent., separating the crystallized 1-naphthalenemonosulfonic acid from the remaining solution, fusing said 1-naphthalenemonosulfonic acid with a caustic alkali, and isolating 1-naphthol from the resulting fusion product.

4. A process for the production of 1-naphthol which comprises mixing naphthalene with sulfuric acid of about 95 per cent concentration, maintaining the temperature of the mixture between 15° and 30° C., causing 1-naphthalenemonosulfonic acid to crystallize from the reaction mixture, continuing the sulfonation with continued crystallization of 1-naphthalenemonosulfonic acid for at least 3 hours after all of the naphthalene has been mixed with the sulfuric acid, while maintaining the temperature at about 15° to 30° C., separating the 1-naphthalenemonosulfonic acid from the remaining solution, and fusing said naphthalene monosulfonic acid with a caustic alkali.

5. A process for the production of 1-naphthol which comprises adding about one part by weight of naphthalene to 3 to 4 parts by weight of sulfuric acid of about 100 per cent concentration, while maintaining the temperature between 15° and 30° C., inducing the 1-naphthalenemonosulfonic acid to crystallize when the reaction mixture becomes supersaturated therewith, continuing the sulfonation at a temperature of about 15° to about 30° C. with continued crystallization of 1-naphthalenemonosulfonic acid, the total reaction period being about 10 to about 15 hours, filtering to recover the crystallized 1-naphthalenemonosulfonic acid from the resulting reaction mass, fusing the resulting 1-naphthalenemono-sulfonic acid with a caustic alkali, acidifying the resulting fusion product, and recovering 1-naphthol from the acidified product.

6. A process which comprises sulfonating naphthalene under such conditions that there is produced a reaction mass containing crystallized 1-naphthalenemonosulfonic acid and sulfuric acid but substantially free from 2-naphthalenemonosulfonic acid, and separating the crystallized 1-naphthalenemonosulfonic acid from the remaining reaction mass.

7. A process which comprises sulfonating naphthalene under such conditions that there is produced a mixture containing crystallized 1-naphthalenemonosulfonic acid in admixture with a solution of a naphthalenedisulfonic acid in sulfuric acid, which mixture is substantially free from 2-naphthalenemonosulfonic acid, and separating the crystallized 1-naphthalenemonosulfonic acid from the remaining solution containing the naphthalene-disulfonic acid.

8. A process which comprises sulfonating naphthalene under such conditions that there is produced a mixture containing crystallized 1-naphthalenemonosulfonic acid in admixture with a solution of a naphthalenedisulfonic acid in sulfuric acid, which mixture is substantially free from 2-naphthalenemonosulfonic acid, controlling the acidity of the mixture so that the total acidity, calculated as sulfuric acid, is at least 80 per cent., and filtering the crystallized 1-naphthalenemonosulfonic acid from the remaining solution.

9. A process which comprises sulfonating naphthalene under such conditions that there is produced a mixture containing crystallized 1-naphthalenemonosulfonic acid in admixture with a solution of a naphthalenedisulfonic acid in sulfuric acid, which mixture is substantially free from 2-naphthalenemonosulfonic acid, controlling the acidity of the mixture so that the total acidity, calculated as sulfuric acid, is at least 80 per cent., and filtering the crystallized 1-naphthalenemonosulfonic acid from the remaining solution at a temperature of about 20° to about 25° C.

10. A process which comprises mixing naphthalene with concentrated sulfuric acid, maintaining the temperature of the mixture between 15° and 30° C., causing 1-naphthalenemonosulfonic acid to crystallize from the reaction mixture, continuing the sulfonation with continued crystallization of 1-naphthalenemonosulfonic acid for at least 3 hours after all of the naphthalene has been mixed with the sulfuric acid, while maintaining the temperature at about 15° to 30° C., controlling the acidity of the mixture so that the total acidity, calculated as sulfuric acid, is at least 80 per cent., and filtering the crystallized 1-naphthalenemonosulfonic acid from the remaining solution.

11. A process which comprises adding about one part by weight of naphthalene to three to four parts by weight of sulfuric acid of about 100 per cent concentration, while maintaining the temperature between 15° and 30° C., inducing the 1-naphthalenemonosulfonic acid to crystallize when the reaction mixture becomes supersaturated therewith, continuing the sulfonation at a temperature of about 15° to about 30° C. with continued crystallization of 1-naphthalenemonosulfonic acid, the total reaction period being about 10 to about 15 hours, and filtering the crystallized 1-naphthalenemonosulfonic acid from the resulting reaction mass.

WILLIAM J. COTTON.