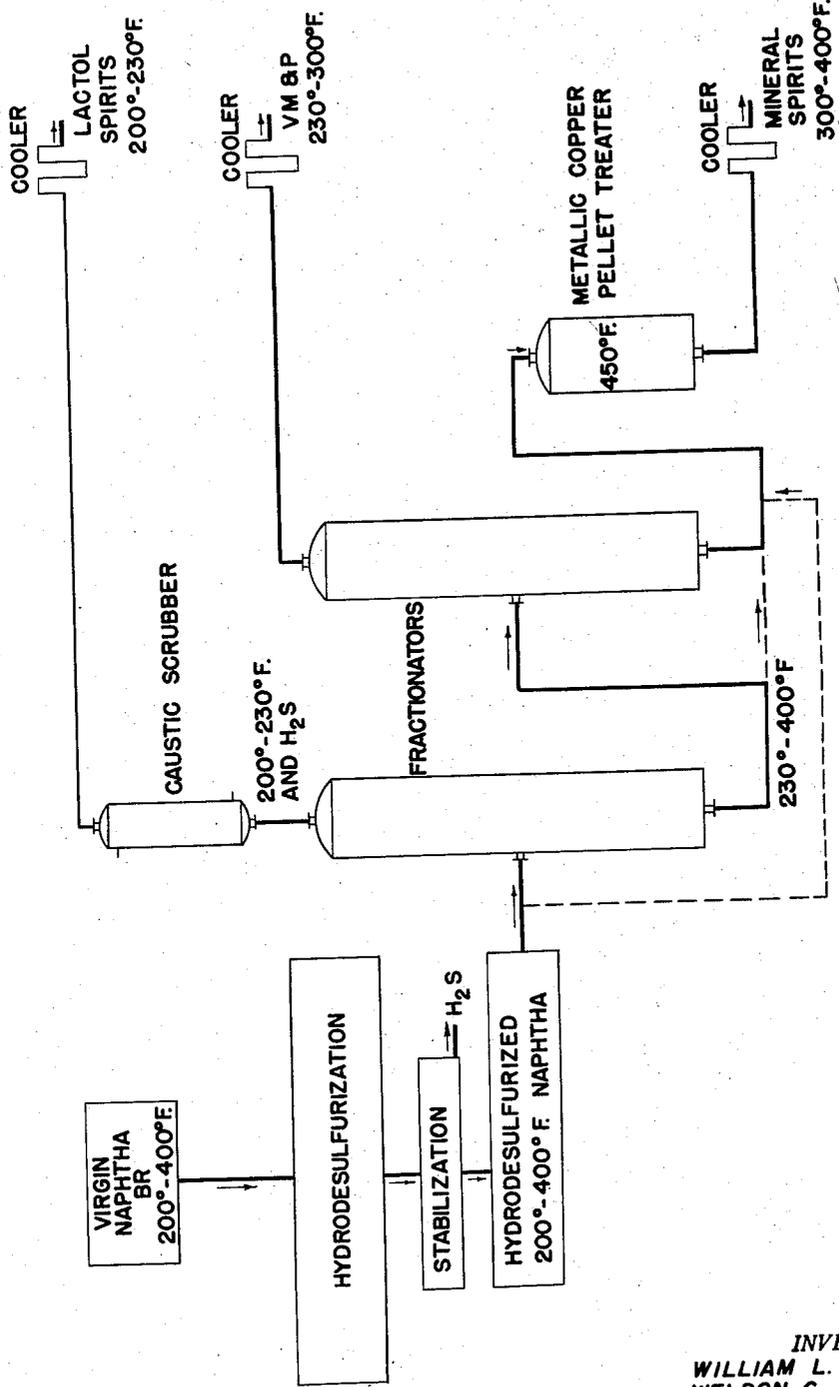


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HYDRODESULFURIZATION OF NAPHTHAS FOLLOWED BY  
TREATMENT WITH EITHER METALLIC  
COPPER OR SILVER  
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## HYDRODESULFURIZATION OF NAPHTHAS FOL- LOWED BY TREATMENT WITH EITHER METAL- LIC COPPER OR SILVER

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The present invention relates to a combination three-  
stage process of catalytic hydrodesulfurization, fractiona-  
tion and chemical treatment of high sulfur petroleum  
hydrocarbon mixtures and, more particularly, to a method  
of treating high or low sulfur stocks or highly aromatic  
stocks to produce improved naphthas characterized by  
their ability to pass the distillation-corrosion test. More  
specifically, the invention relates to an integrated process  
for producing high grade naphthas from hydrocarbon  
mixtures involving a catalytic hydrodesulfurization and  
a chemical treatment of a 300–400° F. fraction therefrom  
with certain metals from group IB of the Periodic Chart  
of the Atoms (Welch, 1941), namely copper and silver.  
The products resulting from the process of this inven-  
tion are to be distinguished from naphthas separated from  
coal tars, and the term "solvent naphtha" used herein is  
intended to mean naphthas which are strictly of petro-  
leum origin or from petroleum hydrocarbon mixtures.

Crude petroleum is the source of a large number of  
products ranging from simple distillation products, in-  
cluding pure hydrocarbons, to high molecular weight  
natural and synthetic resins, elastomers, and polymers  
produced through physical and chemical transformations.  
Widely known petroleum-derived products include gaso-  
line, kerosene, diesel fuels, lubricating oils, and heavy  
tars. In many instances, the products obtained from petro-  
leum are employed as reactants in the synthesis of addi-  
tional petroleum derivatives and chemicals and a large  
number of products of petroleum are used directly with-  
out extended treatment or modification. Petroleum  
naphthas comprise a wide variety of such latter products  
used extensively in the dyeing, rubber, extraction, protec-  
tive coating, and allied industries. A large portion of  
the petroleum naphthas used is the straight-run naphthas  
which are selected fractions of the lower boiling, more  
volatile constituents of crude petroleum. The present  
invention is particularly directed to a method of pre-  
paring such straight-run naphthas, and to naphtha com-  
positions of this variety; accordingly, the term naphthas  
as used herein shall mean straight-run petroleum naph-  
thas. Also, where the term chemical treatment is used, it  
is meant to include both catalytic and non-catalytic con-  
version conditions in vapor, liquid, or mixed phase.

If the preparation of naphthas from petroleum is con-  
fined to physical means, the products inevitably contain  
other types of organic and inorganic compounds due to  
the complex nature of petroleum which have been found  
to be deleterious as far as certain end uses of the naph-  
thas are concerned and necessitate the application of addi-  
tional refining steps. Even with such additional refining,  
it is exceedingly difficult to prepare naphthas which meet  
the exacting specifications that have been established by  
the industry. Of these deleterious non-hydrocarbon com-  
pounds the sulfur and sulfur-containing constituents are

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generally the most difficult to remove and cling tena-  
ciously to any environment in which they exist, imparting  
objectionable odor, corrosiveness, color, and other physi-  
cal and chemical properties thereto. The odor of naph-  
thas is important; however, no standard test exists to  
cover this property and the odor of a well-refined naphtha  
is generally described as sweet.

Tests have been devised to determine both quantitative-  
ly and qualitatively the presence of these odious com-  
pounds in an attempt to control the properties and quality  
of naphthas from petroleum sources. For this purpose,  
various copper strip corrosion tests and the "doctor" test  
have been used. Procedures established by A.S.T.M.  
may be used to determine the content and distribution of  
these sulfur compounds. Perhaps the most critical and  
rigorous qualitative test for determining the presence of  
sulfur compounds in naphthas is the distillation-corrosion  
test, known also as the Philadelphia test, the Amsco  
corrosion test, or the full boiling-range corrosion test—  
by any name, a species of copper strip corrosion test.  
The test, widely applied by the manufacturers, distribu-  
tors, and users of specialty naphthas, is carried out by  
the addition of a small, pure copper coupon to an ordi-  
nary A.S.T.M. distillation flask containing 100 cc. of the  
naphtha to be tested. The copper strip is so positioned  
in the flask that one end of the strip contacts the residue  
at the end of the distillation, and the distillation is con-  
ducted according to A.S.T.M. D86–38 as described in  
A.S.T.M. Standards on Petroleum Products and Lubri-  
cants, published by the American Society for Testing Ma-  
terials, Philadelphia, Pennsylvania.

At the completion of the test, wherein the flask has  
been heated to dryness, the color of the copper strip  
is an indication of the relative amount of corrosive sul-  
fur compounds present in the naphtha sample. A nega-  
tive test is shown by the presence of a very slight or no  
tarnish on the strip and stamps the naphtha as satisfac-  
tory. If the copper strip becomes moderately tarnished  
or blackened, the results are interpreted as positive or  
unsatisfactory. The production of a slightly tarnished,  
or slightly colored or corroded strip indicated by a dark  
orange with peacock colorations thereon, is termed bor-  
derline and as such denotes a naphtha which is not ac-  
ceptable and must be further refined. The market is  
limited for off-specification naphthas and further refin-  
ing is expensive since even then there is no assurance  
that the product will pass the severe distillation-corrosion  
test.

The subjection of high sulfur content naphthas to  
various refining and sweetening operations, which may in-  
clude oxidation and extraction methods, or the recycling  
of rejected off-specification naphthas back through such  
a process, does not produce acceptable naphthas because  
the sulfur compounds remaining are corrosive in nature.  
High sulfur content naphthas usually have a poor odor  
as well as other undesirable properties. If straight-run  
naphthas from high sulfur crudes are subjected to other,  
more severe refining methods, the resulting products do  
not pass the distillation-corrosion test. Even subjecting  
these naphthas to the usual desulfurization treatments  
involving vapor or liquid phase contact with clay or cata-  
lytic materials having strong activity for effecting desul-  
furization does not produce a satisfactory product.  
For example, it is known to be advantageous to suc-  
cessively treat hydrocarbons containing sulfur compounds  
to hydrodesulfurization processes followed by second stage  
treatments which predominate in hydrogenation-dehydro-  
genation. In the first stage hydrodesulfurization, the sul-

fur compounds present in the stock are substantially completely decomposed, with the formation of hydrogen sulfide, and a proportion of the unstable, olefinic hydrocarbons present in the stock or formed during the desulfurization is hydrogenated and converted to more stable compounds. During the second stage, generally conducted in the presence of a catalyst, the predominant reactions are cracking and reforming in the presence of hydrogen under optimum conditions to obtain gasoline products which have high octane numbers and good lead susceptibility. One particular advantage of these prior art processes is that the bulk of the sulfur compounds and the majority of the coke-forming olefins are eliminated in the first stage so that the catalyst in the second stage is not substantially converted to sulfides nor is it subjected to conditions of rapid coke deposition. The products formed are entirely free of hydrogen sulfide and have a very low content of sulfur compounds. Products may be produced containing only 0.009 to 0.016 percent or lower content of sulfur in the form of organic sulfur compounds other than mercaptans in accordance with prior art teachings. Further, it is sometimes the practice, after the desulfurization reaction, to subject the feed to hydrogenation and reforming at temperatures in the range of 950° F. to 1100° F. for the purpose of increasing the value of the products as motor fuel by reason of increased anti-knock rating.

However, these prior art processes cannot be depended upon to produce products which are consistently free of corrosive sulfur compounds as indicated by their ability to pass the distillation-corrosion test because there is a sharp distinction between desulfurization as meant in the prior art and the desulfurization necessary to produce a non-corrosive naphtha. Thus, the desulfurization by whatever method may take place to the extent of 90 to 98 percent sulfur removal, but the products produced will not be non-corrosive and will not pass the critical distillation-corrosion test. On the other hand, desulfurization may be of such nature that non-corrosive naphthas are produced through the conversion of corrosive sulfur compounds to a non-corrosive variety without appreciable total sulfur reduction taking place. It follows, therefore, that certain naphthas may be more corrosive after desulfurization than before, and, further, a naphtha which gives a sour "doctor" test may be non-corrosive while a sweet naphtha may be corrosive.

Accordingly, the primary object of this invention is to provide a three-stage process for producing improved naphthas of good solvency characteristics and low corrosive sulfur content.

Another object is to provide a combination process of three-stage hydrodesulfurization, fractionation and chemical treatment which produces improved naphthas.

A third object of this invention is to provide a method of producing naphthas which pass the distillation-corrosion test.

A fourth object is to provide a combination three-stage hydrodesulfurization, fractionation and chemical treatment using metallic copper or silver in the last stage to produce acceptable, sweet, odor-free, non-corrosive, and substantially sulfur-free special solvent naphthas.

These and other objects will become apparent as the description of the invention proceeds.

The attached drawing is a partially diagrammatic illustration of the flow of materials and apparatus used in the steps of the process.

According to the present invention, the difficulties aforementioned are eliminated in one aspect thereof by subjecting the raw or virgin hydrocarbon feed stocks to catalytic desulfurization in a first stage, followed by stabilization and treatment in a second stage by chemical reaction with copper. Silver may also be used but the cost is prohibitive. The chemical treatment herein-after described in connection with copper, is conducted under relatively mild conditions as compared with the

hydrodesulfurization reaction and in the absence of hydrogen. The products from this treatment may be fractionated into various specialty naphthas or solvents and are characterized principally by their freedom from those types of corrosive sulfur compounds which give a positive distillation-corrosion test. In addition, the products have high solvency power and have a satisfactory odor.

In another aspect of the invention, it has been found that the fractions of the hydrodesulfurized product boiling below about 300° F. (so-called rubber solvent) are non-corrosive and need no further treatment, but the hydrodesulfurized fractions boiling above about 300° F., which are designated as mineral spirits, Stoddard solvent and 140 solvent or heavy naphthas, contain a trace of sulfur or other corrosive sulfur compounds which can be removed or transformed into non-corrosive forms by treatment with copper. It has further been found that the fraction or fractions, whether including the portion boiling below about 300° F. or not, which are subjected to chemical treatment with copper should be substantially free of hydrogen sulfide, mercaptans and disulfides in order to obtain products which pass the distillation-corrosion test and which are of acceptable odor and non-corrosive.

In carrying out the present invention, any hydrocarbon material from which naphthas or solvents or similar products may be obtained can be used wherein the objective is to overcome the tendency toward the formation or carry-over of those types of sulfur compounds which cause a positive distillation-corrosion test. Crude oil is one source of material from which large quantities of solvents and naphthas are produced. It is preferable in order to prolong the life of the treating agent that the more volatile components and the high boiling residues present be removed by fractionation or other methods prior to treatment in accordance with this invention. For example, a crude oil containing from 1.0 to 3.0 or as high as 7.0 weight percent of sulfur is fractionated to obtain a wide-boiling-range virgin or straight-run naphtha having an end boiling point of about 500° F. A gas-oil fraction may be used which boils between about 500° and 700° F. Kerosene fractions may also be used. Preferably, a straight-run naphtha fraction boiling between 110° and 450° F. is treated in accordance with the invention.

The boiling range of the particular fraction removed for treatment in accordance with this invention may be varied somewhat from the boiling ranges given depending upon the relative amounts of specialty naphtha, rubber solvent, V.M. & P., and other naphthas desired. By narrowing the boiling range of the virgin naphtha to within 100° to 250° F., the process may be directed to obtaining rubber solvents almost exclusively. On the other hand, by starting with a fraction boiling between 200 and 400° F., the process may be directed to production of V.M. & P. solvents and specialty naphthas. In one specific embodiment of the invention, the treatment of the entire first fraction, boiling up to 500° F. or more is carried out to produce a wide variety of products ranging from the rubber solvents up to high boiling specialty naphthas including, for example, petroleum ether 90°-140° F., special textile spirits 180°-210° F., light mineral spirits 290°-330° F., Stoddard solvent 310°-385° F., and high flash dry cleaning solvent 360°-400° F., all being non-corrosive, of sweet odor, and meeting the rigorous requirements of the industry.

The virgin naphtha fraction selected from the crude is subjected to a catalytic hydrodesulfurization treatment carried out in accordance with well-known techniques at elevated temperatures. In this process the sulfur content of the charge stock is removed in the form of a gas such as hydrogen sulfide by the action of hydrogen and desulfurization catalysts, such as molybdates, sulfides, and oxides of iron group metals and mixtures including cobalt molybdate, chromic oxide,

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vanadium oxide with molybdena and alumina, and sulfides of tungsten, chromium, or uranium. A preferred catalyst for the reaction is a cobalt oxide-molybdena-alumina catalyst or a chromina-molybdena-alumina catalyst. Commercially available cobalt molybdate catalysts are very suitable for the process. The process may be carried out in either the liquid or gaseous phase at temperatures ranging from 500° to 800° F. and under pressures from 20 to 1000 pounds per square inch. The virgin naphtha fraction subjected to hydrodesulfurization may contain from about 1.0 to about 3.0 percent by weight of sulfur compounds. Generally the types of fractions suitable for the preparation of solvent naphthas will contain from below about 0.1 to 3.0 percent of sulfur compounds. The charge may be introduced to the catalyst zone at from 0.5 to 10 pound volumes per bulk volume of catalyst per hour.

The fraction selected from the crude oil is conducted to the hydrodesulfurization reaction zone, as shown in the diagram, which illustrates the processing of a virgin fraction. The preferred conditions of hydrodesulfurization are approximately 750° F., 250 pounds per square inch pressure, and a space velocity of 0.3 to 2.0, with hydrogen recirculated at a rate of about 3000 s.c.f. of hydrogen per barrel of charge. The reactor may be of the fixed bed or fluidized bed type.

The products from the hydrodesulfurization are subjected to stabilization wherein the hydrogen sulfide and any fixed gases are removed from the liquid product. Removal of hydrogen sulfide from the liquid product can also be accomplished by countercurrent contact with an amine solution. The hydrogen may also be purified by removal of hydrogen sulfide and recycled back to the first stage of the process. The hydrogen sulfide removed may be used to prepare free sulfur. The product from the hydrodesulfurization is either: (1) conducted as is to the chemical reaction zone in which contact is made with copper in free metal form at about 400° to 500° F. under atmospheric pressures, or (2) fractionated to remove the fraction boiling below about 300° F. and subjecting the fraction boiling above about 300° F. to chemical treatment with copper under the same conditions. The conditions of chemical treatment have been found to be rather critical. At temperatures below 400° F. a product passing the distillation-corrosion test is not obtained. At 400° F. contact times may be unduly lengthened. Conducting the process at above about 500° F. results in discoloration of the naphtha and the production of odorous compounds which are not easily removed by known contact or extraction methods. The chemical treatment with copper is optimum at 450° F., which condition gives consistent and reproducible results.

The invention is not to be limited by any theories herein propounded or inherently set forth but it is supposed that the relatively low temperatures in the second stage initiate a combination of catalytic and non-catalytic reactions wherein there is a chemical tie-up of these corrosive sulfur compounds which are detrimental in the end products. Since there is no substantial evidence of any considerable reduction in total sulfur in the process, at least a part of the reaction is the conversion of the deleterious sulfur compounds to forms which do not affect the distillation-corrosion test. Since the second stage reaction is in the absence of hydrogen, no hydrogen sulfide appears in the products. Consequently, there is no need for subsequent stabilization or caustic washing and the effluent from the second stage chemical treatment may be immediately fractionated to yield the desired naphthas. The main reduction of sulfur compounds takes place during the initial hydrodesulfurization, and consequently the life of the copper contact material used in the second stage reaction is sustained.

In order to demonstrate the invention, a series of ex-

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periments was conducted in which a virgin naphtha having the following characteristics:

Gravity	° APL	54.2
Aniline point	° F	135.9
B.R.	° F	210 to 375

Sulfur distribution:

Free-S	Trace
H <sub>2</sub> S-S	Trace
RSH-S	0.012
R <sub>2</sub> S <sub>2</sub> -S	0.003
R <sub>2</sub> S-S	0.005
Residual-S	0.016
Total S	0.036
Doctor test	Pos.
Lead acetate test	Pos.
Mercury test	Pos.
Distillation-corrosion test	Pos.
Vol. percent naphthenes and paraffins	92.0
Vol. percent olefins	1.0
Vol. percent aromatics	7.0

was subjected to hydrodesulfurization at a temperature of 780° F. and 385 p.s.i.g. in the presence of cobalt molybdate and hydrogen. Table I shows the characteristics of the hydrodesulfurized naphtha, the 190-312° F. fraction and the 312-398° F. fraction distilled therefrom.

TABLE I

## Production of non-corrosive naphthas

	Desulfurized naphtha	VM & P, 190-312° F.	Low E. P. Stoddard, 312-398° F.	Copper pellet treated low E. P. Stoddard, 312-398° F.
Vol. percent of desulf. naphtha	100.0	57.7		39.6
Gravity, ° APL	54.2	56.5		49.4
Aniline point, ° F	135.9	135.7		136.8
Distillation-corrosion test	Borderline	Pass	Fail	Pass
ASTM distillation, ° F.:				
IBP	210	233		322
5%	254	249		327
10%	263	252		328
20%	273	255		330
30%	280	258		331
40%	288	261		333
50%	296	265		335
60%	304	268		337
70%	314	272		340
80%	325	277		343
90%	339	285		350
95%	349	290		357
DP	375	298		371
EP		300		371
Rec.	99.5	98.8		98.6
Res.	0.4	1.1		1.2
Loss	0.1	0.1		0.2
Total, sulfur, weight percent	0.005			
Vol. percent naphthenes and paraffins	91.8			
Vol. percent olefins	1.0			
Vol. percent aromatics	7.2			

From Table I it is apparent that the desulfurized naphtha gave "Borderline" results in the distillation-corrosion test. After fractionation, however, it was found that the 190-312° F. fraction passed the distillation-corrosion test but the 312-398° F. fraction failed and gave a positive distillation-corrosion test. When the 312-398° F. fraction was treated with copper pellets at 450° F., the resulting product passed the distillation-corrosion test. If the desulfurized naphtha, before distillation, is allowed to stand or is stored for any length of time, it shows a "borderline" or positive distillation-corrosion test. Borderline products, like those giving a positive test, are not marketable as non-corrosive naphthas.

The 312-398° F. naphtha fraction shown in Table I, which failed the distillation-corrosion test, was divided into five portions and each was subjected to chemical treatment with different treating agents as shown in Table

75 II.

TABLE II

## Treatment of hydrodesulfurized naphtha

Temperature, 460° F.  
Pressure, Atmospheric  
LVHSV, 5  
Liquid recovery, 100%

Treating agent	Silver molybdate	Nickel molybdate	Copper molybdate	Copper oxide <sup>1</sup>	Copper <sup>1</sup>
Volume, cc.....	100	100	100	100	100
Weight, gm.....	99.2	95.3	106.4	267.9	506.7
Distillation-corrosion test.....	Neg.	Neg.	Neg.	Neg.	Neg.
Yield, bbl./ton.....	4,899	7,322	4,184	3,430	5,571
Condition at end of run.....	Spent.	Spent.	Spent.	Spent.	Active.
Regeneration necessary.....	Yes	Yes	Yes	Yes	No.

<sup>1</sup> Pellets.<sup>2</sup> Pellets disintegrated and plugged reactor.

From these experiments it is seen that such chemical treating agents as silver molybdate, nickel molybdate, copper molybdate and copper oxide, although effective in the production of products which pass the distillation-corrosion test, exhibit short active lives and are spent in a short time, making regeneration necessary. In addition, copper oxide disintegrated and plugged the reactor, even though in pelleted form. On the other hand, copper pellets, even after being used for a length of time to yield more non-corrosive naphtha than the silver molybdate, copper molybdate, or copper oxide, was still active and did not require regeneration. In fact, at the end of the experiment using copper, it was found that the loss in weight of the copper pellets was only about 1%, which indicates that copper pellets could be continued in use yield about 10,000 bbl. per ton or more of non-corrosive naphtha. On a cost basis this represents a substantial saving over the molybdate salts and copper oxide with which the comparison was made. It was found that the copper pellets at the end of the experiment were only slightly covered with a sulfide coating which flaked off leaving the metal exposed. The sulfide coating cannot be regenerated to the metal. However, by mechanical removal of the flakes of copper sulfide from the pellets the treating agent is ready for reuse if desired.

Referring to the drawing which shows the process diagrammatically, the process of the invention may be carried out as follows: A virgin naphtha having a boiling range of about 200 to 400° F. is subjected to hydrodesulfurization at temperatures ranging from about 500 to 800° F. and under pressures from about 20 to 1000 lbs. per square inch, using a catalyst selected from the group consisting of cobalt oxide-molybdena-alumina, chromia-molybdena-alumina and cobalt molybdate-alumina or cobalt molybdate alone. The hydrodesulfurization is carried out under conditions whereby sulfur compounds within the naphtha are converted to hydrogen sulfide. The major portion of the hydrogen sulfide may be removed in a stabilization step by caustic washing or extraction with an amine solution. The hydrodesulfur-

ized naphtha is next subjected to fractionation in one or more fractionators, as in a first stage fractionation wherein a 200 to 230° F. fraction along with any remaining hydrogen sulfide is removed as overhead, and a 230 to 400° F. is recovered as bottoms. The 200 to 230° F. fraction is subjected to caustic scrubbing to produce lactol spirits. During the second fractionation a V.M. and P. fraction boiling in the range of 230 to 300° F. is removed as overhead, and a 300 to 400° F. fraction is removed as residue. This latter fraction, qualified as mineral spirits, is subjected to treatment with metallic copper pellets in a treater at temperatures to 400 to 500° F., and preferably about 450° F., to produce a non-corrosive product which passes the distillation-corrosion test.

As an alternative procedure, all of the 200 to 400° F. naphtha may be subjected to chemical treatment with copper. Also, all of the 230 to 400° F. fraction may be subjected to chemical treatment before further fractionation. This is indicated by the dotted by-pass lines in the diagram.

Although the invention has been illustrated by various experiments, the only limitations attaching thereto appear in the appended claims.

What is claimed is:

1. The process for producing naphthas which pass the distillation-corrosion test from hydrocarbon mixtures of petroleum origin containing deleterious sulfur compounds which comprises separating a virgin naphtha fraction containing below about 0.1 to 3.0 percent by weight of sulfur compounds and having a boiling range of about 200° to 400° F. from said hydrocarbon mixture, subjecting said virgin fraction to hydrodesulfurization at a temperature of about 780° F. in the presence of hydrogen and a catalyst capable of promoting hydrodesulfurization, separating a hydrogen sulfide-free hydrodesulfurized product containing about 0.005 weight percent total sulfur compounds, subjecting said hydrodesulfurized product to fractionation to recover a fraction boiling between about 300° to 400° F., subjecting said 300° to 400° F. fraction to contact with a free metal selected from the group consisting of copper and silver at a temperature of 450° F. in the absence of hydrogen and recovering a naphtha product characterized by its ability to pass the distillation-corrosion test.

2. The method in accordance with claim 1 in which the virgin naphtha contains about 0.036 weight percent total sulfur compounds and said hydrodesulfurization catalyst is cobalt molybdate.

3. The method in accordance with claim 1 in which said contacting agent is copper in the form of pellets.

4. The method in accordance with claim 1 in which said contacting agent is silver in the form of pellets.

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