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**PRODUCTION OF NAPHTHAS PASSING THE
DISTILLATION-CORROSION TEST**

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This invention relates to a method for preparing improved petroleum naphthas and industrial solvents. The method especially relates to the production of light distillate petroleum fractions suitable for industrial use which are noncorrosive to metallic surfaces in contact therewith at moderately elevated temperatures.

Selective fractions of mixed hydrocarbons comprising the lighter, more volatile constituents of crude petroleum, which are commonly called petroleum naphthas, have long been provided by the petroleum industry to meet the demands and needs required by a wide variety of industrial uses. Although there are available from other industries, such as the coal tar industry, various naphthas, this invention is directed to the preparation of petroleum naphthas and any reference hereinafter made to naphthas unless a contrary intention is shown will be construed to mean naphthas produced from crude petroleum oils. From a small assortment of naphthas such as rubber solvent, varnish makers and painter's naphtha and Stoddard solvent, due to the advent of superfractionating equipment employed as naphtha rerun units, there has developed a wide variety of superfractionated, close boiling range naphthas having a myriad of applications in the natural and synthetic rubber industry, protective coating industry, extraction industry, as well as other miscellaneous applications. This plurality of applications has necessitated the evaluation of the numerous characteristics of petroleum naphthas such as dilution ratio, sulfur content, color, odor, volatility, flash point, solvency, and corrosion so that one having a need for a naphtha for a particular purpose may specify that the naphtha comply with certain specifications which are correlated with the foregoing properties. Accordingly tests have been devised which establish standards to insure compliance with the stipulated specifications and to facilitate understanding between the producer and consumer. Test results provided by these tests are given interpretations which are indicative of whether or not the naphtha tested is a satisfactory product. As a measure of the corrosive effect of the naphtha, because of dissolved free sulfur or sulfur compounds contained therein, the distillation-corrosion test, the copper strip corrosion test, and the doctor test have been devised to indicate the presence of sulfur compounds which might attack metals or cause the darkening of paints or varnishes.

It is therefore an object of my invention to prepare light petroleum hydrocarbon distillates which are non-corrosive to metals sensitive to corrosion by various sulfur-containing materials.

It is a further object of my invention to prepare a petroleum naphtha which will give a satisfactory result when subjected to the test environment encountered in the distillation-corrosion test.

These and other objects will be made apparent in the following detailed discussion of my invention.

Although pure hydrocarbons from petroleum are available petroleum naphthas and solvents do not generally consist of a pure single chemical but are a homogeneous

mixture of many hydrocarbons. Therefore the generally used naphthas can be classified as (1) straight run petroleum naphthas which consist essentially of aliphatic and naphthenic hydrocarbons, and (2) highly aromatic petroleum naphthas. The straight run naphthas are prepared by controlling the distillation range of the various light distillates available from the distillation of crude petroleum. While these distillates may be obtained in the atmospheric distillation of crude petroleum employed in "topping" operations as side stream cuts without further ado, in order to make naphthas which will meet consumer specifications based upon their particular demands the various distillates are refractionated in naphtha rerun units thereby producing the special naphtha fractions which have a wide variety of uses. The aromatic naphthas are generally prepared by methods which increase the aromatic content of the naphtha over that which was originally present by subjecting the naphtha to aromatization and cyclization reactions which occur in processes such as hydroforming or the like or by extraction with SO₂ of distillates from highly aromatic crude petroleum oils.

The crude petroleum oils from which the petroleum naphthas are produced determine to a certain extent the properties and characteristics of the naphthas prepared therefrom. This is particularly exemplified in the naphthas produced from a low sulfur content or "sweet" crude and those prepared from a high sulfur type or "sour" crude. The light distillate products produced from the latter generally contain hydrogen sulfide and other sulfur compounds which give the product a bad odor or render them quite corrosive to metals. Such distillates are likewise termed "sour" and to prepare a marketable product it is necessary to employ remedial measures for overcoming these noisome and deleterious properties in the form of treating processes which will finish the product to established standards of quality.

Due to the desulfurization characteristics of the processes utilized in the manufacture of highly aromatic naphtha, aromatic naphthas are normally sulfur-free. However if any sulfur-containing constituents are contained therein they are of such a nature that a light treating operation is sufficient to remove them and satisfactory products prepared with a minimum of finishing operation. Straight run naphthas contain deleterious sulfur compounds which must be removed or rendered harmless in order to provide a marketable product.

Accordingly treating systems are employed in conjunction with naphtha rerun units whereby the feed stock to or the product from the naphtha rerun unit is treated to reduce or modify the sulfur content of the distillate. Light distillates produced as side streams from the crude distillation unit are also similarly treated without subsequent refractionation in a rerun unit. The hydrogen sulfide contained in the naphthas can be removed by extraction with aqueous solutions of sodium hydroxide. More drastic treatment however must be employed in the modification or removal of the organic sulfur compounds contained in the untreated naphtha. Numerous processes have been developed which are employed in treating light petroleum distillates and therefore adaptable to naphtha treating operations. These processes are classified in three broad groups: (1) oxidation, which chemically convert the mercaptans to disulfides, also called "sweetening." Examples of this type are the doctor treat, copper chloride, hypochlorite processes, and catalytic oxidation employing polyhydroxy phenolic compounds as catalysts. (2) Sulfur removal which physically extract the mercaptans from the hydrocarbon distillate but do not materially effect the other sulfur compounds. Processes which the prior art describes as effecting the

removal of mercaptans are the Mercapso process, Solutizer process and the Unisol process, and (3) acid, clay and catalytic processes which remove some or all of the different types of sulfur compounds. Inasmuch as sulfur content, odor and corrosion of petroleum naphthas are related certain criteria have been established to determine the effect of sulfur and sulfur compounds in naphthas. These criteria take the form of qualitative determinations, the results of which are indicative of the effect of any free or combined sulfur in the naphtha. It has been pointed out that three applicable qualitative tests have been developed to make these determinations, namely, the copper strip corrosion test, the doctor test and the distillation-corrosion test. The doctor test and the copper strip test are widely used throughout the petroleum industry and have been provided with ASTM designations D 484-40 and D 130-30, respectively, and descriptions thereof may be found in the publication "ASTM Standards on Petroleum Products and Lubricants." Where the noncorrosiveness of the petroleum naphtha is of primary concern in the selection of an appropriate naphtha the doctor test is inferior for the detection of corrosive sulfur compounds in comparison with the tests employing a copper strip, viz., distillation-corrosion test and copper strip corrosion test. In the latter test a copper strip is placed in a sample of the petroleum naphtha being tested and the sample held in a suitable bath at 122° F. for 3 hours. Although the purpose of this test is to detect free sulfur and corrosive sulfur compounds in light distillates, because of the relatively low temperature employed, the test is not applicable to indicate the potential corrosiveness of sulfur compounds present due to the decomposition of the sulfur compounds, said decomposition occurring when the naphtha is subjected to elevated temperatures encountered in processes such as solvent recovery systems thereby producing corrosive sulfur-containing materials. Therefore a more rigorous test, which is not only critical of the corrosive effect of sulfur and sulfur compounds inherently present in the light distillate or which have remained in a treated petroleum naphtha but is also responsive to the corrosive effect of those sulfur-containing materials which occur in the naphtha due to the decomposition of the sulfur constituents of petroleum naphtha at temperatures encountered, is the distillation-corrosion test. Although this test is variously known as the Amsco corrosion test, the full flask distillation test, the full corrosion test, the procedure is standardized and is widely used in the manufacture and sale of special naphthas. While a description of this test, which hereinafter will be referred to as the Distillation-Corrosion test, is to be found in an article by L. M. Henderson, et al. entitled "The effect of sulfur and sulfur compounds in naphtha upon certain corrosion tests," Industrial Engineering Chemistry, Analytical Edition, 12 (1) 1, the test in essence employs a modification of the standard method of test for distillation of gasoline, naphtha, kerosene and similar petroleum products, ASTM designation D 86-46, wherein a clean strip of polished pure sheet copper about ½" x 3" and of sufficient thickness to stand lengthwise without buckling is placed into the regulation distilling flask and exactly 100 cc. of the naphtha to be tested is placed therein. The naphtha sample is distilled in accordance with the manner prescribed in the foregoing ASTM distillation test D 86-46, the copper strip remaining in the flask during the entire distillation. At the completion of the distillation the copper strip is allowed to cool in the flask to room temperature before it is taken from the apparatus. In the interpretation of the results of this Distillation-Corrosion test a slight tarnish on the copper strip does not indicate that the material has not satisfactorily met the test. However any marked blackening of the copper strip means that the material is unsatisfactory. In accordance with the condition of the copper strip if the naphtha tested is not

corrosive the result is reported as "negative" and if it is corrosive the result is reported as "positive."

Naphtha as treated in the various treating or sulfur removing processes outlined above will normally be an odorless and "sweet" product because of the absence of free sulfur and hydrogen sulfide, and negligible mercaptan content. However these "sweet" light petroleum products when subjected to the Distillation-Corrosion test may not give a satisfactory "negative" result due to the dissociation of the sulfur compounds remaining in the treated naphtha into corrosive sulfur-containing products. It is also found that the residual sulfur compounds per se in a treated or untreated product may produce a "positive" result. When such a petroleum naphtha is encountered it is necessary to retreat the once treated naphtha in order to prepare a satisfactory and marketable material. On occasion a naphtha product is manufactured which fails to respond to this retreatment and the refiner has the problem of rechanneling an unsatisfactory product into a market in which there may occur an economic disadvantage.

I have found a method which obviates these unprofitable aspects whereby a petroleum naphtha which fails to yield a satisfactory "negative" result when subjected to the Distillation-Corrosion test is blended with a proportion of a naphtha exhibiting satisfactory "negative" results with reference to the Distillation-Corrosion test. The product resulting from this blending procedure is a marketable petroleum product which is noncorrosive to copper and which will successfully pass the Distillation-Corrosion test. This product is prepared without the necessity of retreating the petroleum naphtha to remove those constituents which are the cause of the "negative" Distillation-Corrosion test.

The sulfur compounds which are present in a sweet petroleum naphtha which is produced from a "sweet" crude petroleum oil or a "sour" petroleum crude oil which necessitates subsequent treating usually are sulfides and disulfides and mercaptans, some of the mercaptans and all of the hydrogen sulfide having been removed in the treating process. The mercaptans present are relatively unstable substances when exposed to moderately high temperatures and break down to form hydrogen sulfide, olefins and other products. The organic sulfides are somewhat more stable to heat than the corresponding mercaptans and while most of the disulfides present in naphtha solutions are apparently stable at moderate temperatures when naphthas containing these sulfur compounds are subjected to the temperatures encountered in the Distillation-Corrosion test, some decomposition is effected and very corrosive products are formed. Mercaptans (traces), sulfides and disulfides are noncorrosive per se and if a light petroleum product containing these constituents conforms to other specifications relating to odor, color, etc., the presence of these materials does not prevent such a composition from having consumer acceptance. Therefore if a petroleum naphtha containing these sulfur compounds is subjected to the Distillation-Corrosion test and the boiling point of the said sulfur compounds is sufficiently low that they may be distilled over with the naphtha without decomposition no corrosion of the copper strip contained in the fraction is evinced and a "negative" test result obtains which is indicative of a satisfactory product. However, when the boiling point of the said sulfur compounds is sufficiently above the end point of the naphtha being tested the sulfur compounds remain in the distillation residue and at the moderately high temperatures encountered in the test, some decomposition of the sulfur compounds and attendant corrosion of the copper strip results thereby indicating a product which may be otherwise acceptable is non-acceptable because of its corrosiveness. I have found that this decomposition can be precluded and a naphtha having a desired boiling range and being satisfactory from a corrosion standpoint prepared by blending as much

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as 90% of a light hydrocarbon distillate, which by itself gives a poor result in the Distillation-Corrosion test and 10% of a second petroleum fraction which has a slightly higher boiling range than the other constituent of the blend and furthermore gives a satisfactory "negative" result in the Distillation-Corrosion test. The higher boiling material which is added to the original light hydrocarbon distillate has the property of facilitating the distillation of the sulfur compounds which would otherwise tend to accumulate in the distillation residue and cause the naphtha to produce a negative result with reference to the Distillation-Corrosion test due to the decomposition of the said sulfur compounds. By this means it is possible to produce naphthas which will conform to the corrosion specifications thereby producing satisfactory naphthas from fractions of crude oils which would otherwise be unsuitable for the production of naphthas.

A more tangible presentation of my invention is described as follows: a Stoddard solvent having a boiling range from about 300° F. to about 400° F. may be prepared from a light distillate fraction obtained from a West Texas crude petroleum oil, said fraction having a boiling range of approximately 300° F. to about 390° F. This light distillate fraction although treated in one of the conventional treating systems produces a positive result when subjected to the Distillation-Corrosion test. To 90 parts by volume of this treated material is added 10 parts by volume of a light hydrocarbon fraction boiling in the range between about 380° F. to about 400° F. range. This latter constituent is obtained from a low sulfur content crude oil or from a process which produces a product which is noncorrosive as indicated by the negative results obtained when this said fraction is tested with the distillation-corrosion procedure. The blend thus prepared will pass the Distillation-Corrosion test because the sulfur compounds inherently present are distilled over with the naphtha without decomposing. Since the sulfur compounds are not permitted to accumulate in the distillation residue no decomposition is effected which would result in the forming of products which would corrode the copper strip employed in the test. The foregoing example is intended merely to be illustrative of my invention and it is to be understood that my invention is not confined to the use of the proportions of hydrocarbon fractions mentioned therein. It is, however, essential to my invention that the fraction employed in the blend which is noncorrosive to copper when tested in the Distillation-Corrosion test be the higher boiling component of the blend and that a sufficient amount of the noncorrosive higher boiling fraction be used so that the distillation employed in the Distillation-Corrosion test may be effectuated without decomposition of the sulfur compounds contained in the blend thereby preventing the corrosion of the test strip of copper employed as an indicator in the test. Regarding the relative amounts of the high boiling constituent of the blend, the maximum amount employed is determined by the economics of the finished products and the distillation characteristics of the blend. The minimum amount utilized must be determined experimentally as the crude oils used to produce the blend constituents, type of sulfur compounds, and relative amounts thereof as well as other factors, function to influence and provide the corrosive properties of the petroleum distillates employed as blend constituents. It will be noted that in the foregoing example a West Texas crude was employed in manufacturing one of the blend constituents. To overcome the deleterious corrosive properties of the light distillate produced therefrom it was necessary to provide 10 parts by volume of a sweet, higher boiling, noncorrosive petroleum distillate to produce a satisfactory product. If the light distillate were prepared from a Worland, Wyoming or other high sulfur containing crude the relative proportions of the blend constituents might vary from this ratio. This determination must be made experimentally. In carrying out my inven-

tion a naphtha which is noncorrosive to copper can be prepared as a blend of several naphthas in which the constituents are present in various proportions. In order to produce a naphtha which will give a negative test result with reference to the Distillation-Corrosion test it is only necessary that a sufficient quantity of the blend constituent having the highest boiling range and which exhibits negative results when subjected to a Distillation-Corrosion test be added so that when a sample of the thus prepared naphtha blend is tested in the Distillation-Corrosion test there will be sufficient bottoms in the flask during the carrying out of the test so as to cause essentially all of the deleterious sulfur compounds to be distilled over with the naphtha thereby preventing their decomposition and resultant corrosion.

No necessary precautions relative to this invention are necessary in the blending operation. The blending procedures variously used throughout the petroleum refinery industry to produce blends of light hydrocarbon distillate may be employed.

Thus it will be seen that my invention consists of the preparation of a marketable naphtha in an economical manner from a light hydrocarbon fraction which itself cannot be used for the purposes for which it was prepared. The test employed to indicate the enhanced effect that is obtained by my blending method is not an integral part of the invention but is merely a criteria which has been established to facilitate the determination of whether or not the product of my invention will conform to the rigorous noncorrosive requirements demanded by consumers of industrial naphthas and solvents.

I claim:

1. A method for producing a petroleum aliphatic naphtha which when subjected to the Distillation-Corrosion test will produce a satisfactory negative result, which consists essentially of blending about 90% by volume of an oxidatively sweetened straight run naphtha distillate which gives an unsatisfactory positive result in the Distillation-Corrosion test, with about 10% by volume of a second, sweet, higher boiling range naphtha fraction in an amount to produce said petroleum naphtha, said second naphtha fraction exhibiting satisfactory negative results with reference to said Distillation-Corrosion test and having said boiling range in which the initial boiling point is substantially the same temperature as the end point of the first light hydrocarbon distillate and having an end point temperature equal to the desired end point temperature of the said petroleum naphtha.

2. A method for preparing an aliphatic petroleum naphtha product having a boiling range of from about 300° F. to about 400° F., said product yielding satisfactory negative results when subjected to the Distillation-Corrosion test, which consists essentially of blending 90 parts by volume of an oxidatively sweetened straight run naphtha distillate having a boiling range from about 300° F. to about 390° F., said distillate being produced from a West Texas crude petroleum oil and providing unsatisfactory results in the Distillation-Corrosion test, with 10 parts by volume of a sweet naphtha fraction having a boiling range from about 380° F. to about 400° F., said fraction exhibiting a satisfactory negative result in the Distillation-Corrosion test, to produce said petroleum hydrocarbon product.

3. A method for producing an aliphatic petroleum naphtha which is non-corrosive to metals sensitive to corrosion by sulfur-containing materials as determined by the Distillation-Corrosion test, said naphtha having as a constituent a major portion of an oxidatively sweetened straight run naphtha distillate free from sulfur-containing materials selected from the group consisting of elemental sulfur, hydrogen sulfide and polysulfides containing more than two sulfur molecules in the polysulfide linkage and containing sulfur compounds selected from the group consisting of mercaptans, organic sulfides and organic disulfides, said sulfur compounds being sub-

ject to form upon thermal decomposition corrosive sulfur-containing products which produce a positive result with reference to the Distillation-Corrosion test, which consists essentially of blending said naphtha distillate with a minor portion of a second sweet, non-corrosive straight run naphtha fraction having an initial boiling point lower than the end boiling point of said naphtha distillate and an end boiling point higher than the end boiling point of said naphtha distillate, said second naphtha fraction being characterized by providing negative test results with reference to the Distillation-Corrosion test, in an amount sufficient to produce a homogeneous blended aliphatic petroleum naphtha which is non-corrosive to metals sensitive to sulfur corrosion at temperatures not substantially greater than the end boiling point of said aliphatic petroleum naphtha.

4. A method for preparing an aliphatic petroleum naphtha which is non-corrosive to metallic surfaces contacted thereby at temperatures not substantially exceeding the end boiling point of said petroleum naphtha, which comprises subjecting a crude petroleum oil to distillation and separating therefrom a sulfur-containing naphtha distillate, treating said naphtha distillate in an oxidation sweetening process to convert the mercaptans contained therein to disulfides thereby producing a product which is doctor sweet but which produces positive results when subjected to the Distillation-Corrosive test, distilling a second petroleum crude oil and recovering therefrom a second naphtha fraction, said second naph-

tha fraction being a sweet product which yields negative results when subjected to the Distillation-Corrosion test and having a lower initial boiling point and a higher end boiling point than the end boiling point of said naphtha distillate, and blending a minor portion of said second naphtha fraction with a major portion of said naphtha distillate, said second naphtha fraction being present in an amount sufficient to produce an aliphatic petroleum naphtha which yields negative results with reference to the Distillation-Corrosion test.

5. A method in accordance with claim 4 in which the second naphtha fraction is obtained from the distillation of a crude petroleum oil, said distillation being carried out in the presence of copper oxide.

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