Patented Jan. 8, 1952

2,582,192

UNITED STATES PATENT OFFICE

2,582,192

DIESEL FUEL OIL

George H. Denison, Jr., San Rafael, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Application July 13, 1948, Serial No. 38,553

5 Claims. (Cl. 44—57)

1

This invention relates to an improved diesel fuel oil, and more particularly to improved diesel-fuel-oil compositions containing a small amount of a highly effective gum-inhibiting additive.

As is known, a deposit commonly called "gum" may collect on the filters of diesel engines when using many of the known diesel fuel oils. The gum formation may also give rise to injection valve clogging with the resulting inefficient motor operation. It may cause complete engine failure. Even in the milder forms of gum depositing, almost constant maintenance is required. An object of this invention is to provide a diesel fuel-oil composition with a reduced tendency toward gum formation.

In order to increase the "middle-of-the-barrel" yield of crude petroleum, various refining processes have been employed by the refining industry which increase the yield of useable products. Although this processing greatly increases the valuable product yield, it gives rise to gum content in the petroleum products. Accordingly, another object of this invention is to provide a diesel fuel-oil composition that does not form gum when the base stock of this composition has been subjected to refining processes.

With the increasing use of high-speed diesel engines, higher ignition quality (cetane number) diesel fuel oils are required. Whereas formerly a cetane number of 25 was thought to be adequate, engineering advancements have brought about the requirement, in many instances, of cetane numbers above 50. Cetane-improving additives are quite often necessary in compounding these diesel fuel oils. Cetane-improving additives for diesel fuel oil include the following types of materials: alkyl nitrites and nitrates; nitro and nitroso bodies; aldehydes; cyclic hydrocarbon peroxide; ketone peroxides; polysulfides, such as dialkyl polysulfides; tertiary peroxides; di-(tertiary alkyl) peroxides; tetralin peroxides; and tertiary alkyl hydroperoxides. Among the peroxides and hydroperoxides specifically mentioned as cetane-improving additives for diesel fuel oil are: di-isobutane peroxide; di-isopentane peroxide; di-2-methyl butane peroxide; di-2-ethyl butane peroxide; di-2-methyl pentane peroxide; di-3-methyl pentane peroxide; di-2,3-dimethyl butane peroxide; di-2,4-dimethyl butane peroxide; di(tertiary butyl) peroxide; and di(tertiary amyl) peroxide. Additional di(tertiary alkyl) peroxides mentioned are: di(methyl-2-pentyl-2) peroxide; di(methyl-3-pentyl-3) peroxide; di(ethyl-2-butyl-2) peroxide; di(halo-1-methyl-2-propyl-2) peroxide; di(halo-1-ethyl-2-

2

propyl-2) peroxide; di(halo-1-methyl-2-butyl-2) peroxide; di(halo-1-methyl-3-butyl-3) peroxide; di(halo - 2 - methyl - 3 - butyl - 3) peroxide; di-(phenyl - 1 - methyl-1-propyl-1) peroxide; and di(phenyl - 1 - methyl - 2 - propyl - 2 - peroxide. Among cyclic hydrocarbons mentioned as cetane-improving additives are: cyclopentyl hydroperoxide, methylcyclopentyl hydroperoxide, the isomeric dimethylcyclopentyl hydroperoxides, ethylcyclopentyl hydroperoxide, the isomeric diethylcyclopentyl hydroperoxides, the isomeric methylethylcyclopentyl hydroperoxides, cyclohexyl hydroperoxides, methylcyclohexyl hydroperoxide, the dimethylcyclohexyl hydroperoxides, ethylcyclohexyl hydroperoxide, the three isomeric diethylcyclohexyl hydroperoxides, 1–4 methylisopropylcyclohexyl hydroperoxide, peroxides of cyclobutane, cycloheptane, etc., and higher molecular weight substituted-cycloparaffins. In addition, another peroxide cetane-improving additive is disclosed in the Schultz et al Patent No. 2,317,968 and is prepared by partially oxidizing a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, and of a higher volatility than kerosene with an oxygen-containing gas under liquid-phase conditions at a temperature of 275 to 310° F. for a sufficient length of time to produce an oil having an oxygen factor (obtained by adding excess KI to the oil sample, then titrating the liberated iodine with $Na_2S_2O_3$ and then calculating the results according to the equation: titer in ml. × normality of the thiosulfate × 1120/volume of sample in ml.) higher than 800, but insufficient to increase the neutralization number of the oil by more than 20, then arresting said treatment before the oxygen factor of the produced oil decreases to below about 800 and then removing the acidic reaction products from the produced oil without reducing the oxygen factor to below about 800. The patent of Denison, No. 2,521,698, discloses another peroxide type cetane-improving material prepared by subjecting a petroleum distillate having a boiling range between 200 and 450° F. and relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds to a liquid-phase oxidation treatment with an oxygen-containing gas at a temperature within the range of 200 to 400° F. for a period of time sufficient to produce an oil having an oxygen factor higher than 250; contacting the resulting oxygenated oil with 0.1 to 0.75 pound of 50–90 per cent H_2SO_4 per gallon of oil at a temperature of 50 to 85° F. for less than

90 minutes, thereby producing a more stable and less corrosion-producing oil having a substantially lowered oxygen factor, treating this oil with controlled amounts of weak caustic solution to remove acidic material, and concentrating the caustic-treated oil by fractional distillation at a temperature below 350° F. and a pressure between 10 mm. of mercury and atmospheric to volatilize between 60 and 95 per cent of said oxygenated oil to obtain a concentrate of relatively stable cetane-improving oxygenated oil. This patent of Denison further discloses that the additive may be used as a cetane-improving additive in ordinary diesel fuel in amounts between 0.2% to 25% of the base, fuel, desirably between about 1% and 15%, especially between 2% to 8% of the base fuel. The addition of additives of this type quite often results in the compounded fuel having an abnormally large gum depositing tendency. Thereby, it is a further object of this invention to provide a diesel fuel oil composition that does not form gum when cetane-improving compositions are added to it.

It has been discovered that the addition of homologous heterocyclic reduced nitrogen bases prepared from petroleum nitrogen bases will effectively prevent the formation of gum when added to diesel fuel oil; that these reduced nitrogen bases will prevent the formation of gum when added to diesel fuel oils having a gum-forming tendency and which contain cetane-improving additives; and that they will prevent gum formation when added to a refined diesel fuel oil.

One method of preparing these reduced nitrogen bases or secondary amines as they are sometimes called, according to the Rutherford Patent No. 2,302,655, is by extracting a crude, nitrogen-base-containing petroleum distillate boiling in the boiling range of gasoline, naphtha, or kerosene, cracked or uncracked, with a dilute mineral acid to form water-soluble salts of mixed nitrogen bases; separating these salts from the oil; then neutralizing these salts which converts them to crude nitrogen bases. Thereafter this product is hydrogenated at an elevated temperature and pressure in the presence of a sulfactive hydrogenation catalyst to form homologous, heterocyclic, secondary amines or, as they are sometimes called, reduced nitrogen bases of naturally occurring petroleum nitrogen bases.

According to the Rutherford patent, a crude cracked naphtha, as obtained in the pyrogenetic cracking of a nitrogen-containing crude petroleum oil or distillate, is extracted at ordinary temperatures with a dilute aqueous sulfuric acid solution, of a concentration generally below about 50% H_2SO_4 and preferably about 30% H_2SO_4; water-soluble sulfates of mixed petroleum nitrogen bases are formed. The aqueous solution of these salts is separated from the petroleum oil, by decantation, and the mixed petroleum nitrogen bases are recovered by decomposing the salts with a dilute aqueous alkali metal hydroxide solution, added to the dilute sulfuric acid solution of the basic salts in slight excess; the bases thus recovered are sufficiently water-insoluble to permit of stratification and decantation. In a typical case, a mixture of the crude bases thus separated from a crude cracked 100°–500° F. naphtha of California petroleum origin had a specific gravity of 0.943, a basic dissociation constant of 4.0×10^{-8}, an average molecular weight of 150, and an A. S. T. M. distillation boiling point range (method D–86) between 360° and 478° F. (20% point, 382°; 50% point, 398; 90% point, 442° F.); it had a sulfur content of 0.15% and was 99% soluble in an equal volume of 30% sulfuric acid.

The mixed nitrogen bases thus recovered are reduced to secondary amines by passage over molybdenum sulfide, MoS_3, suitably deposited on activated charcoal, in the presence of hydrogen and at superatmospheric temperature and pressure, accompanied by an active sulfur carrier such as carbon disulfide. In the above typical case, the crude mixed nitrogen bases referred to were passed over the catalyst at a rate of 0.3 volume of liquid bases/volume of catalyst space/hour at an average catalyst temperature of 505° F., accompanied by hydrogen fed at the rate of 33 moles/mol of bases and also accompanied by carbon disulfide fed at the rae of 1% by weight of the bases; the catalyst chamber was maintained 3000 pounds per square inch hydrogen pressure. After condensation and cooling, the whole reaction mixture is adjusted to a pH of approximately 9.5 by the careful addition of dilute aqueous sulfuric acid solution, upon which the reduced bases pass into aqueous solution as salts and the unreduced bases and produced neutral oil remain water-insoluble. The two layers thus formed are separated by decantation and dilute aqueous alkali metal hydroxide solution is added to the aqueous solution of the reduced salts, thus converting them to secondary amines which are sufficiently water-insoluble to permit of stratification and removal by decantation. In the above typical case, 56% by weight of the mixed bases were recovered as unreduced bases, and 8% were recovered as hydrocarbon oil. The characteristics of the secondary amines were: specific gravity, 0.849; basic dissociation constant, 1.0×10^{-3}; average molecular weight, 146; A. S. T. M. distillation boiling point range, 340° F. (20% point, 360°; 50% point, 366°; 90% point, 386° F.); solubility in 30% sulfuric acid, 100%.

In further exemplification of the several operating variables in the process as described:

The temperature of reduction is best maintained at between about 475° and about 535° F.; 500°–510° is optimum. At lower temperatures, conversion is incomplete; the table, based on operations conducted upon crude bases extracted from cracked petroleum naphtha, indicates that at higher temperatures the nitrogen base heterocyclic nucleus is destroyed, yielding large amounts of hydrocarbons (and ammonia):

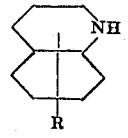
Maximum Oven Temperature	Average Oven Temperature	Reduced Bases	Unreduced Bases	Oil
		Percent	*Percent*	*Percent*
514	482	43	50	7
535	505	56	37	7
603	560	38.5	42.5	19
660	613	45	5	50

In general, increased hydrogen pressure improves the rate and degree of reduction, and a low space rate (volume liquid bases/volume catalyst/hour) is in most cases preferable. Best results are obtained when feeding about ten times the theoretically required proportions of hydrogen, that is, when feeding about 30 moles hydrogen per mol of cracked petroleum nitrogen base rather than the theoretically required 3 moles per mol, and when feeding up to about 50 moles hydrogen per mol of uncracked petroleum nitrogen base rather than the theoretically required 5 moles per mol. The table illustrates the relation-

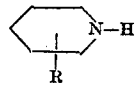
ships between space rate, hydrogen feed and degree of reduction, in a system maintained at 200 atmospheres hydrogen pressure and oven temperature of 505° F., in operations carried out on cracked petroleum nitrogen bases.

Space Rate	Hydrogen Feed		Bases reduced	Bases Unreduced	Oil
	Moles/mol	Cu. ft./bbl.			
			Percent	*Percent*	*Percent*
0.3	11	10,000	38	35	27
0.3	22	20,000	47	47.5	5.5
0.3	33	30,000	56	35.5	8.5

It is generally believed that the nitrogen bases extractable from straight-run distillates are alrgely mixture of alkylated quinoline homologues and that those extracted from cracked distillates are largely alkylated pyridine homologues. Upon reduction in the manner hereinabove described, these bases are believed to yield mixtures of secondary amines, respectively, typified by the following structures:



and



in which the heterocyclic nuclei are saturated and in which R represents one or more alkyl groups attached in the alpha, beta or gamma positions (probably the beta); R apparently has an average of about 5 carbon atoms per molecule, but individual members of this homologous series may carry alkyl groups containing from one to about eight carbon atoms per chain.

The existence of nitrogen bases in many crude petroleums and in their cracked and straight-run distillates has been known for some time. These compounds have been removed at the refinery, as they were throught to be an undesirable impurity. It was recently discovered, however, that, by proper processing, nitrogen bases of crude petroleum could be reduced to stable secondary amines. As nitrogen bases are generally found in most crude petroleum and since their recovery is relatively simple, their use as a gum-inhibiting additive is economically advantageous in addition to being highly effective. This is especially true, as a small amount gives such worth-while results.

Through experimentation it has been discovered that generally a maximum amount of about five per cent and usually about two-tenths per cent of the reduced nitrogen bases derived from petroleum (based on volume of diesel fuel oil), is sufficient to prevent gum-formation during storage or when used in diesel engines. It has been found that amounts from 0.05 per cent to 0.5 per cent ordinarily give satisfactory results. It is to be understood, however, that when the diesel fuel oil has an unusually high gum-forming tendency, a greater amount of the reduced nitrogen bases may be necessary to prevent gum formation.

The term "diesel fuel oil" as used herein includes straight-run or cracked petroleum distillates boiling in the range of about 325° F. to about 750° F.

The mechanism of gum formation in diesel fuel oils is not definitely known. No theory has been firmly established, though a large number of investigators have worked on this problem. As a result of these investigations, an oxidation theory was advanced to account for gum formation in petroleum products. In some degree, this theory has been accepted. In conformity with this theory, many so-called antioxidant additives have been employed, with varying success, to prevent gum formation in the gasoline and diesel fuel oil fractions. However, this theory of gum formation does not apparently apply to diesel fuel oils, as evidenced by the following experiment: A diesel fuel was completely stripped of oxygen (air) by passing nitrogen through it. Thereafter, this stripped diesel fuel oil was heated to 250° F. in a sealed tube for 20 hours. A gum deposit soon formed, thus showing that oxidation is not the sole gum-forming mechanism. It appears probable that gum formation in this stock is the result of polymerization.

That the oxidation theory will not explain gum formation in distillates of the diesel fuel oil boiling range is further indicated by the experiments summarized in Tables I and II. Table I gives the results when reduced nitrogen bases and well-known antioxidants were added to a California straight-run distillate boiling in the diesel fuel oil range, containing the cetane-improving additive disclosed in the Schultz et al. Patent No. 2,317,968. Table II gives the results when reduced nitrogen bases and the cetane-improving additive disclosed in the Denison Patent No. 2,521,698, were added to a different (than that used in Table I) California straight-run distillate boiling in the diesel fuel oil range. In each test a measured amount of the gum-inhibiting additive and the cetane-improving additive was added to a weighed flask containing 100 ml. of the distillate which was then heated for 20 hours at 250° F. Gum formation was measured by decanting the oil out of the flask, washing with petroleum ether, drying, and then weighing the flask. This weighing determined the amount of gum adhering to the flask.

Table I

Gum-Inhibiting Additive, Kind	Cetane-improving Additive of U. S. Patent 2,317,968, Vol. percent	Gum Inhibiting Additive's Amount Vol. percent	Milligrams of Gum	
			Run 1	Run 2
None			23	23
None	3		51	53
50% Isobutyl para-amine phenol, 30% isopropanol, and 20% methanol (commonly sold as du Pont Antioxidant No. 6)	3	0.2	53	57
N,N' disecondary butyl paraphenylene diamine (commonly sold as Universal Oil Products' Antioxidant No. 5)	3	0.2	37	32
Reduced Nitrogen Bases	3	0.2	5	6

From this foregoing table it is apparent that examples of typical antioxidants, when employed as gum inhibitors in diesel fuel oils compounded with cetane improvers, are not effective gum inhibitor additives. This is in contrast to the fact that the reduced nitrogen bases substantially decreased gum formation in the compounded diesel fuel oil.

Table II

Gum-Inhibiting Additive, Kind	Gum-Inhibiting Additive, Vol. percent	Cetane-Improving Additive of Patent No. 2,521,698, Vol. percent	Milligrams of gum	
			Run 1	Run 2
			13	19
		1	35	36
Du Pont Antioxidant No. 6	0.2	1	[1] 42	[1] 40
Universal Oil Products' Antioxidant No. 5	0.2	1	[1] 15	[1] 20
Reduced Nitrogen Bases	0.2	1	1	3

[1] Additional amounts of gum formed but did not adhere to the flask.

Again in this table as in Table I, it is evident that the reduced nitrogen bases are effective gum inhibitors in these compounded diesel fuel oils, whereas inhibition of gum is not accomplished by the so-called antioxidant type gum inhibitors. With this in mind, it appears that oxidation is not the gum-formation mechanism in distillates boiling in the diesel fuel oil range.

Another factor, from which it may be reasonably concluded that the oxidation theory of gum formation does not wholly apply to diesel fuel oil, is that these peroxide-type cetane-improving additives and the petroleum reduced nitrogen bases are compatible. This compatibility characteristic is illustrated by the fact that peroxygenated hydrocarbon cetane-improving additives and the reduced nitrogen petroleum bases can coexist in a diesel fuel oil without appreciable interaction. Likewise, each can perform its primary function in the presence of the other as if it were alone in the diesel fuel oil composition. On the other hand, when compounded diesel fuel oils were made with a diesel fuel oil, a peroxygenated hydrocarbon cetane-improving additive, and an antioxidant type gum inhibitor, apparently appreciable interaction occurred between the two additives. This interaction gives rise to a diesel fuel oil tending to have the same cetane number and gum-depositing characteristic as the diesel fuel oil had before being compounded.

The following examples further illustrate the effectiveness of reduced nitrogen bases prepared from petroleum nitrogen bases to suppress the formation of gum in diesel fuel oil.

Example I

Two 100 cc. samples of a California crude straight-run petroleum distillate having a boiling range of 340 to 590° F. were added to tared 125 cc. Erlenmeyer flasks. To one of these flasks was added 0.2 cc of reduced nitrogen bases prepared from petroleum nitrogen bases as described hereinabove. The flasks were immersed in a 250° F. constant-temperature oil bath for 20 hours. After 20 hours had elapsed, the flasks were removed from the bath and allowed to cool at room temperature for one hour. The oil was then decanted from the flasks and thereafter the flask was washed by decantation with successive 25 cc. portions of petroleum ether and allowed to dry with the increase in weight indicating formation of gum. The flask containing only the distillate had 14 mg. of gum; while the flask having 0.2 cc. of reduced nitrogen bases added to it had only 1 mg. of gum.

This result shows the suppression of formation of 13 mg. of gum per 100 cc. of distillate.

Example II

This test was conducted in the same manner as Example I. Likewise, the petroleum used in this sample had the same boiling range as the one used in the first example. A quantity of this fuel was mixed with one per cent, by volume, of the cetane-improving additive disclosed in the Denison patent described above. A 100 cc. sample of this compounded fuel was added to each of two tared 125 cc. Erlenmeyer flasks. To one of these flasks was added 0.2 cc. of reduced nitrogen bases prepared from petroleum nitrogen bases as described above. When these flasks were weighed after the heating, cooling, and washing period, it was found that the flask having the reduced nitrogen bases did not contain gum. The other flask, however, contained 38 mg. of gum.

From the results of this test, it is apparent that 0.2 per cent of reduced nitrogen bases suppressed formation of 38 mg. of gum per 100 cc. in the compounded diesel fuel oil.

In a similar test, the cetane-improving additive disclosed in the Schultz et al. patent described hereinabove was substituted for the cetane-improving additive of the Denison patent with comparable results being obtained. Similar results may be obtained with diesel fuels to which the other peroxides and hydroperoxides listed above have been added to raise the cetane number. Similar results may also be obtained with diesel fuels containing non-peroxide cetane-improving additives listed above such as the alkyl nitrates and nitrites.

While various specific embodiments of the invention have been illustrated and described, many modifications and adaptations may be made without departing from this invention, and all such changes as are included within the scope of the claims are embraced thereby.

I claim:

1. An improved diesel fuel oil containing essentially a major portion of a diesel fuel oil having a substantial gum-depositing characteristic and a minor portion sufficient to inhibit formation of gum of reduced petroleum nitrogen bases comprising a homologous mixture of heterocyclic secondary amines having a basic dissociation constant higher than 1.0×10^{-4} prepared by extracting a crude petroleum oil fraction containing nitrogen bases with a dilute mineral acid to form water-soluble salts of mixed nitrogen bases, separating the salts from the petroleum oil fraction, neutralizing the salts to convert them to crude nitrogen bases, hydrogenating the bases at an elevated temperature and pressure in the presence of a sulf-active hydrogenation catalyst to form reduced petroleum nitrogen bases.

2. An improved diesel fuel oil consisting essentially of a major portion of a diesel fuel oil, a minor portion not exceeding 5 per cent of an oxygenated petroleum distillate having an oxygen factor not below about 800 prepared by partially oxidizing a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds and of a higher volatility than kerosene with an oxygen-containing gas under liquid-phase conditions at a temperature of 275 to 310° F. for a sufficient length of time to produce an oil having an oxygen factor higher than 800 but insufficient to increase the neutralization number of the oil by more than 20 and then arresting the said treatment before the oxygen factor of the produced oil decreases to below about 800, and re-

moving the acidic reaction products from the produced oil without reducing the oxygen factor to below about 800, and a further minor portion sufficient to inhibit formation of gum of reduced petroleum nitrogen bases comprising a homologous mixture of heterocyclic secondary amines having a basic dissociation constant higher than 1.0×10^{-4} prepared by extracting a crude petroleum oil fraction containing nitrogen bases with a dilute mineral acid to form water-soluble salts of mixed nitrogen bases, separating the salts from the petroleum oil fraction, neutralizing the salts to convert them to crude nitrogen bases, hydrogenating the bases at an elevated temperature and pressure in the presence of a sulf-active hydrogenation catalyst to form reduced petroleum nitrogen bases.

3. An improved diesel fuel containing essentially a major portion of a diesel fuel oil, at least 1 per cent by volume and not exceeding five per cent by volume of a relatively stable cetane-improving oxygenated oil prepared by subjecting a petroleum distillate boiling in the range of 200 and 450° F. relatively free from asphaltic and resinous materials and large proportions of aromatic ring compounds to a liquid-phase oxidation treatment with an oxygen-containing gas at a temperature within the range of 200–400° F. for a period of time sufficient to produce an oil having an oxygen factor higher than 250, then contacting the resulting oxygenated oil with 0.1 to 0.75 pound of 50–90 per cent H_2SO_4 per gallon of oil at a temperature of 50 to 80° F. for a period less than 90 minutes, thereby producing a more stable and less corrosion-producing oil having a substantially lowered oxygen factor, treating this oil with controlled amounts of weak caustic solution to remove acidic material and then concentrating the caustic treated oxygenated oil at a temperature below 350° F. and a pressure between 10 mm. of mercury and atmospheric to volatilize between 60 and 95 per cent of said oxygenated oil by fractional distillation, and at least 0.2 and not over 5 per cent by volume of reduced petroleum nitrogen bases comprising a homologous mixture of heterocyclic secondary amines having a basic dissociation constant higher than 1.0×10^{-4} prepared by extracting a crude petroleum oil fraction containing nitrogen bases with a dilute mineral acid to form water-soluble salts of mixed nitrogen bases, separating the salts from the petroleum oil fraction, neutralizing the salts to convert them to crude nitrogen bases, hydrogenating the bases at an elevated temperature and pressure in the presence of a sulf-active hydrogenation catalyst to form reduced petroleum nitrogen bases.

4. An improved diesel fuel oil comprising a major proportion of a diesel fuel oil and a minor proportion of reduced nitrogen bases comprising a homologous mixture of heterocyclic secondary amines obtained by extracting nitrogen-base-containing petroleum hydrocarbon oils with dilute mineral acid to form water-soluble salts of mixed nitrogen bases, separating the salts from the petroleum oil fraction, neutralizing the salts to convert them to crude nitrogen bases, and hydrogenating the bases at an elevated temperature and pressure in the presence of a sulf-active hydrogenation catalyst.

5. An improved diesel fuel oil comprising a major proportion of a diesel fuel oil and a minor proportion of the order of 0.05 to 5% by volume of reduced petroleum nitrogen bases prepared by extracting nitrogen-base-containing petroleum hydrocarbon oils with dilute mineral acid to form water-soluble salts of mixed nitrogen bases, neutralizing the salts to convert them to crude nitrogen bases, and hydrogenating said bases at an elevated temperature and pressure in the presence of a sulf-active hydrogenation catalyst to form reduced petroleum nitrogen bases.

GEORGE H. DENISON, JR.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,110,078	Burwell	Mar. 1, 1938
2,302,655	Rutherford	Nov. 17, 1942
2,317,968	Schultz	Apr. 27, 1943
2,363,012	Miller et al.	Nov. 21, 1944
2,456,569	Smith	Dec. 14, 1943
2,521,698	Denison, JR., et al.	Sept. 12, 1950