

# Refining of Gasoline and Kerosene by Hypochlorites<sup>1</sup>

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*Sulfur, though often present in relatively very small proportions, is the most objectionable impurity in motor fuel, and it is with the removal of sulfur that the present paper deals, although it should be pointed out that the refining method here described does a great deal more than merely remove sulfur. This method is not an academic process, but has been in successful large-scale operation for a little over one year and is now in operation in several refineries.*

*The advantages of the hypochlorite process for the refining of gasoline and kerosene, which are pointed out in this discussion, may be summarized as follows:*

*1—Lower refining cost.*

*2—Less loss on refining, adding materially to the total money saved.*

*3—No acid sludge is formed and no acid to be recovered.*

*4—The operation can be carried out in ordinary steel apparatus; one year's experience has shown that the corrosion of apparatus, piping, etc., is much less than when acid is employed. Lead-lined apparatus is not required.*

*5—The sum total of operation is easier to carry out than the acid-refining process with the acid recovery, etc., incident to the latter.*

*6—It is applicable to the light distillates from all types of crude petroleum.*

IT WAS inevitable that with the tremendous growth of the petroleum industry and particularly the production of gasoline for motor cars, considerable attention would be given to better methods of refining. Considerable impetus has been given to this general problem by the automobile industry and, during the war, by the necessity of finding superior motor fuels and lubricants for aeroplanes. Petroleum refiners, or at least their sales departments, have also come to realize that superior goods are appreciated by the consumer.

The question of good motor fuel is certainly one of universal interest. This country, owning 85 per cent of all the automobiles in the world, produced 5,145,000,000 gal. of gasoline in 1920. At certain seasons the demand has been so great and the lapse of time from the production of gasoline at the refinery to its consumption has been so brief that refiners have often sacrificed everything to "through put." Shipments of gasoline from America to England, Australia, South Africa, and other points, have sometimes had to be returned to be re-refined, or have led to money settlements of no small magnitude. The export of gasoline to foreign countries requires that such gasoline be better refined than is the custom for domestic consumption. The utilization of high sulfur crude oils for gasoline production, the rapid increase in the production of "cracked" gasoline, the relatively insignificant production of very high-grade crudes, such as light Pennsylvania oil, the known merit of benzene in motor gasoline, and the very large losses resulting in the refining of crude benzene, have also been factors in the search for better refining methods.

Although the proper refining of gasoline involves more than the removal of sulfur compounds, the removal of such compounds can, nevertheless, be taken as a fair index of the degree of refining. The nature of the sulfur compounds present in a crude petroleum, or its distillates, makes a great deal of difference, for example, with respect to odor (mercaptans) and corrosive properties, but comparatively little is known as to their exact nature. Figures for the percentage of sulfur in unrefined gasoline distillates are not generally available, but average about one-tenth of the amount present in the original crude petroleum. The percentage of sulfur in a number of crude oils is given in the following table:

CRUDE	PER CENT SULFUR
Persia	1.0
California	0.55 to 3.55
Illinois	0.40 (average)
Louisiana (Jennings)	0.40 to 0.57
Indiana	0.72 to 1.26
Ohio (Lima)	0.65
Texas, Beaumont	0.94 to 2.40
Texas, San Antonio	1.52 to 2.02
Texas, Reeves County	1.00
Texas, Medina County	2.09
Texas, Travis County	1.26
Mexico	1.9 to 4.8

Engler and Höfer give the following sulfur contents of crude petroleum:

CRUDE	SULFUR PER CENT	CRUDE	SULFUR PER CENT
Tegernsee	0.044	Pechelbroun	0.650
Olheim	0.580	Wietze	0.58
Galicia	0.21	Roumania	0.170
Montechine	0.045	Bi-bilibat	0.220
Balachany	0.147	Palembang	0.212
Java	0.473	Sumatra	0.066
Roem Koot	1.166	Pennsylvania	0.049
Burmah	0.121		

Persian crude oil contains about 1.02 per cent and Burmah (Yenan Yung and Singu) about 0.1 per cent sulfur.

Free hydrogen sulfide has been identified in the crude petroleum from Canada, Ohio, Texas, Galicia, and Persia.<sup>2</sup> The natural gas accompanying sulfurous crudes sometimes contains upwards of 10 per cent of hydrogen sulfide. The hydrogen sulfide which frequently appears during distillation is probably partly expelled from solution and partly results from the decomposition of sulfur compounds in the oil.

*Free Sulfur*—Elemental sulfur has been recognized by Richardson and Wallace<sup>3</sup> in Texas petroleum, which, after being freed (at ordinary temperatures) from hydrogen sulfide and filtered through kaolin, deposited crystals of this element.

The natural gas accompanying petroleum rich in sulfur is usually rich in hydrogen sulfide, and the slow evolution of dissolved hydrogen sulfide from certain crudes has apparently been the cause of no small number of fatalities. Kraemer and Spilker<sup>4</sup> state that the presence of sulfur in petroleum is due to activity of certain bacteria, contemporaneous with the algae which these authors regard as the source of petroleum. It is well known that sulfur reacts readily with

<sup>1</sup> Presented before the Section of Petroleum Chemistry at the 64th Meeting of the American Chemical Society, at Pittsburgh, Pa., September 4 to 8, 1922.

<sup>2</sup> Mabery, *Proc. Am. Acad. Arts Sci.*, **31** (1894), 1743; Thiele, *Chem.-Zig.*, **25** (1901), 433.

<sup>3</sup> *J. Soc. Chem. Ind.*, **27** (1902), 316.

<sup>4</sup> *Ber.*, **35** (1902), 1212.

hydrocarbons to give hydrogen sulfide, and Friedmann<sup>5</sup> has shown that thiophenes are also formed. It is not difficult to conceive that such reactions have occurred in nature and would afford an explanation of the presence of sulfur derivatives in petroleum. However, a strong explanation against this explanation is the fact that thiophenes are rarely found in petroleum and then only in traces. Free sulfur is frequently observed in the neighborhood of petroleum wells, and it is not unlikely that this occurrence is due to reduction of sulfur compounds—e. g., mineral sulfates—by the oil or its antecedents. The observations of Steinkopf<sup>6</sup> that acetylene when passed over heated pyrites yields thiophene and that butadiene in a similar way generates methyl thiophene are of interest, though there is no satisfactory evidence of the occurrence of an appreciable quantity of acetylene, butadiene or thiophenes in crude petroleum. Speaking broadly, the thiophene compounds present in petroleum are distributed between all the fractions of the oil, but usually the larger proportion is found in the heavier distillates and particularly in the residues. Thus Perkin<sup>7</sup> describes an American crude containing 0.727 per cent sulfur:

Fraction	Per cent Sulfur	Specific Gravity
to 90° C.	0.02	
110–150° C.	0.10	0.7282
152–220° C.	0.38	0.7669
220–257° C.	0.41	0.7940
257–300° C.	0.37	0.8138

Another oil from Petrolia, Canada, containing 0.98 to 1.06 per cent sulfur gave the following results:

Fraction	Per cent Sulfur	Fraction	Per cent Sulfur
115–150° C.	0.28	250–300° C.	0.51
150–200° C.	0.42	300–350° C.	0.86
200–250° C.	0.50	Residue	0.70

#### ELIMINATION OF SULFUR FROM PETROLEUM DISTILLATES

It has long been established that sulfur compounds occurring in petroleum products are objectionable, and are largely responsible for the properties which refining seeks to remove. While this statement applies to nearly all<sup>8</sup> petroleum products, it is particularly true of gasoline and kerosene. The offensive odors possessed by most unrefined gasolines are due chiefly to very small proportions of mercaptans, and perhaps to a lesser extent to nitrogen bases and simple naphthenic acids. Unrefined gasolines are also usually corrosive to metal, copper being usually employed for the test, and this also is attributed to sulfur derivatives or perhaps to dissolved elementary sulfur. Gasolines and kerosene of offensive odor also usually show a positive "Doctor" test (with alkaline litharge solution). In addition to the effects of sulfur just mentioned, the use of high sulfur gasolines, particularly benzene blends which are apt to have a high percentage of sulfur, results in the formation of acids on combustion in a motor, and this causes serious corrosion. The discoloration and development of acidity in gasoline that is stored for some time is also frequently attributed to sulfur compounds, although these effects are certainly more pronounced in the case of cracked oils which have been refined by sulfuric acid, as pointed out below. Sulfur is probably not such a serious impurity in kerosene as in gasoline, although it is known to cause filming of lamp chimneys and charring and uneven burning of the wick. It is also probably responsible for discoloration during storage.

The best known and one of the most successful processes for desulfurizing oils is the Frasch process, developed to sweeten the so-called "skunk" oils of northern Ohio, Indiana, and

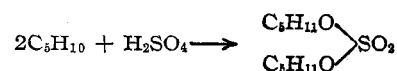
Ontario. The production of this crude has now sunk to very insignificant proportions, and other oils which are now of the greatest industrial importance—for example, the high sulfur Mexican oils—cannot be successfully desulfurized by the Frasch method. Frasch also took out a patent<sup>9</sup> for *dechlorinating* oil which had been treated with bleaching powder. The Frasch method of dechlorinating consisted in heating the oil with alkaline litharge or Doctor solution, but so far as the authors are informed this process was never operated on an extensive scale. Colin and Amend<sup>10</sup> patented a method of refining petroleum distillates which consisted in treating the oil with hypochlorites in the presence of catalytic agents, such as manganese, nickel, or cobalt salts, which evolve oxygen from the hypochlorite. However, the only desulfurizing process other than that of Frasch which has been employed on a large scale is the alkaline litharge method; but, like the Frasch method, this process eliminates only certain classes of sulfur derivatives and is of little or no value on distillates from certain crudes. It is frequently noted that gasolines may be negative to the alkaline litharge test and yet show very marked corrosion of copper and rapid discoloration on standing.

The method of refining by dilute hypochloric solutions described below seems to be universally applicable to desulfurizing all the gasoline and kerosene distillates from all types of crudes. For example, it can be successfully applied to the desulfurizing and refining of naphtha from Mexican crudes, which are not amenable at all to the Frasch method. It should be pointed out also that under the conditions as defined below no chlorine is introduced into the oil. Refining by hypochlorite can be carried out according to either of two principles: (1) complete desulfurization, or (2) refining so as to pass the usual tests and be satisfactory as regards odor, color, and keeping qualities. The latter method requires the employment of much less reagent and is accordingly cheaper. Although the copper corrosion and Doctor tests may be negative and the oil may be quite satisfactory in other respects, not all the sulfur present is actually removed; the corrosive and offensive sulfur compounds present are converted to very stable compounds which are odorless and noncorrosive. The amount of hypochlorite required to refine the gasoline distillate from the average American crude petroleum is remarkably small.

The savings effected by the hypochlorite method vary widely with different oils and according to the degree to which the refining is carried out. Thus, a good quality of crude gasoline distillate may be refined to pass the corrosion and Doctor tests with only 2 or 3 lbs. of chlorine in the form of hypochlorite per 1000 gal., but complete desulfurization of a gasoline, such as that from Persian crude, requires about 1 lb. of chlorine per 50 gal.

#### REFINING OF CRACKED DISTILLATES

It is probable that labile sulfur compounds in oils that have been treated by sulfuric acid are responsible for discoloration when such oils are permitted to stand; this is particularly true of gasoline which has been made by thermal cracking methods and which has been refined by sulfuric acid. When small proportions of sulfuric acid are employed for treating such cracked gasoline, it is possible to bring about a substantial increase in the sulfur content, the sulfur thus introduced being in the form of alkyl esters of sulfuric acid, formed according to the equation—using amylene as an example—



<sup>5</sup> Ber., 49 (1916), 1344, 1551.

<sup>6</sup> Ann., 403 (1914), 11.

<sup>7</sup> J. Inst. Petroleum Tech., 3 (1917), 229.

<sup>8</sup> The presence of sulfur appears to be an advantage in the case of residuum, which is to be blown by air for conversion to asphalt; sulfur accelerates the process, producing a harder product in a given time.

<sup>9</sup> U. S. Patent 525,811 (1894).

<sup>10</sup> U. S. Patent 723,368 (1903).

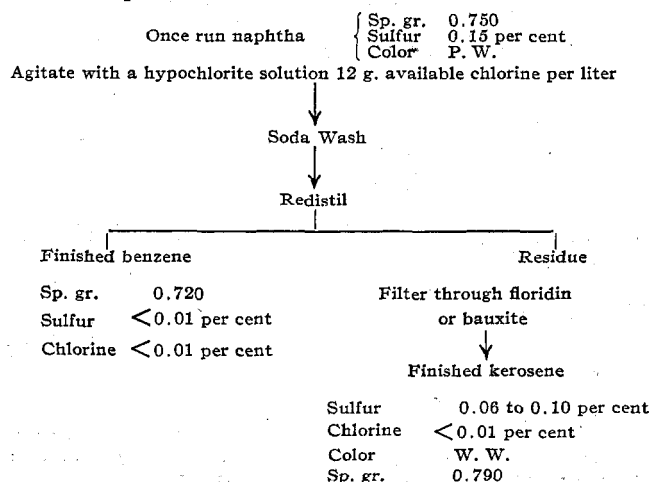
Such esters are not readily removed from the oil by washing with alkali; and it is common experience that such oils, treated in this way, yield free sulfur dioxide when redistilled, even when the alkali wash has been as effective as possible.<sup>11</sup> On the other hand, if large proportions of sulfuric acid are employed for treating, large losses result, varying from about 3 per cent up to 20 per cent, the latter figure being about the average loss on treating Scotch shale oil distillates with sulfuric acid. Very large losses are also experienced in refining crude benzene losses by solution and polymerization frequently amounting to 20 per cent. However, it is now very generally recognized that simple olefins are not objectionable as constituents of motor fuel. It has accordingly become the almost universal practice to refine such cracked naphthas with a small proportion of acid and then redistil to free the gasoline of the sulfuric esters and polymers formed by the acid.

The total loss on refining cracked gasoline, however, is always greater than the observed loss of volume, since a large proportion of the unsaturated hydrocarbons are polymerized to higher boiling hydrocarbons. (When such cracked distillates are not redistilled they quickly become discolored on standing, even for a comparatively short time, and frequently develop a brown sediment and a strongly acid reaction.) This procedure obscures the actual total loss of gasoline. Since polymerization is the principal result with unsaturated hydrocarbons above hexylene in the olefin series,<sup>12</sup> the polymerization loss on treating cracked gasoline is always greater than the observed solution loss. Thus, a cracked gasoline giving a solution loss of 3 per cent will have a polymerization loss of at least an equal amount, or a total gasoline loss of at least 6 per cent. This point is worth emphasizing, because it is by no means universally recognized to be a fact. A number of cracked gasolines made by distilling Oklahoma fuel oil under 100 to 150 lbs. pressure showed polymerization losses of 15 to 30 per cent and the dry point was not reached at 260° C. (500° F.). Although these particular gasolines contained a higher percentage of unsaturated hydrocarbons than commercial cracked distillates made to-day, and were treated with more acid, they do demonstrate that such losses are very real and may be comparatively large. This is still further demonstrated by the action of ordinary concentrated sulfuric acid, 66° Bé., on a mixture of amylenes and hexylenes at -5° C., in which case the loss by solution in the acid was only 11 per cent, but 75 per cent of the mixture was converted into high boiling polymers. Small proportions of acid may bring about a very extensive polymerization. Thus, a pure olefin,  $C_{12}H_{24}$ , of known purity, showed a loss to 85 per cent sulfuric acid of only 4.4 per cent and was almost entirely polymerized; ordinary 96 per cent acid gave a loss of about 10 per cent, and the remainder was *completely* polymerized. The highest solution losses occur in the lighter fractions containing amylenes and hexylenes. In view of the facts just mentioned, it is certain that a careful investigation of the polymerization losses in the present American practice, of refining cracked gasoline by sulfuric acid and redistilling, are very real and probably amount to 3 to 6 per cent of the gasoline treated. The refining of such cracked gasolines by filtering through fuller's earth or similar material also is known to effect some polymerization, and therefore loss, but treatment in this manner has not been very successful or widely adopted. The only published data bearing on this are those of Gurwitsch<sup>12</sup> who noted that amylene was rapidly polymerized by fuller's earth. The refining of such cracked gasoline, including the removal of sulfur compounds, by hypochlorite solutions is by far the most economical method of refining such products.

That the hypochlorite method of refining petroleum distillates had not been worked out many years ago is probably due to the fact that the first attempts resulted in introducing chlorine into the oil. The natural conservatism surrounding a long-established process (sulfuric acid and soda refining), together with the fact that only in recent years has liquid chlorine become a really cheap, bulk staple of the chemical industries, have also been factors in retarding the development and adoption of the new method. Special methods for the cheap and safe transportation of liquid chlorine have also been developed—i. e., specially designed tank cars—and consequently liquid chlorine has rapidly been replacing bleaching powder among consumers of large quantities of bleach.

The active agent in the new process is probably hypochlorous acid. As originally carried out, the hypochlorite solution was generated by the partial electrolysis of salt in specially designed hypochlorite cells. This is unsatisfactory on account of the low utilization of salt, cost of current, rapid deterioration of the cells, and other difficulties which have been the common experience with such cell installations, and the hypochlorite solution is better made up from liquid chlorine, which greatly simplifies the operation and necessary supervision.

The sulfur derivatives in petroleum distillates are rapidly oxidized by dilute hypochlorite solutions, 2 hrs. being the time allowed in the case of the Persian distillates. A concentration of 12 to 15 g. of available chlorine per liter is employed and agitation is accomplished by circulating the aqueous solution through centrifugal pumps discharging below the surface of the oil. The agitators are iron and are not lead lined, experience having shown that corrosion of the iron agitators does not proceed beyond a slight filming of the metal. Part of the sulfur is removed in the form of oxidation products soluble in water. The best procedure, when it is desired to eliminate the sulfur, is to refine the crude naphtha distillate containing both the gasoline and kerosene, then steam-distil the gasoline and pass the kerosene residue through a filter containing dehydrated bauxite or similar adsorbing material to remove the slight color. The oxidized sulfur compounds are much more readily removed by the bauxite than in their original condition. The combined losses amount to about 0.5 per cent in the case of Persian oil, and the refining losses on the same oils as formerly treated by sulfuric acid were 3 per cent. The spent hypochlorite solution is practically a 1 per cent solution of calcium or sodium chloride, and can be disposed of without causing stream pollution or other nuisance. This procedure thus avoids the recovery of acid, burning the acid tars, or other troublesome methods of caring for the acid wastes involved in the old sulfuric acid process.



<sup>11</sup> Brooks and Humphrey, *J. Am. Chem. Soc.*, **40** (1918), 822.

<sup>12</sup> *J. Chem. Soc. (London)*, **1915**, 938.