Modern Gasoline Refining

C. D. Lowry, Jr.

Universal Oil Products Company, Chicago, Ill.

The production of cracked gasoline now exceeds that of straight run and it has become the dominant motor fuel. This is in striking contrast to the conditions when cracking was first introduced. Cracked gasoline only with difficulty secured a place in the gasoline market. Its odor was not like that of straight run, it was yellow in color and it had a tendency to form gum.

Cracked gasoline could not be kept down, however, as it was soon found to be vastly superior to most straight run gasolines in antiknock value. The development of high compression motors of superior performance depended upon the availability of gasoline of high antiknock rating. In the great advances the automotive industry has made in recent years the provision of superior motor fuel by cracking has played a leading part.

At first cracked gasoline was heavily refined to make it look like the straight run product. Eventually, however, it was recognized that most of this refining simply wasted chemicals and caused loss of part of the gasoline. Insistence on water white color was found to be a useless fetish, as it makes no difference to a motor whether gasoline is white or yellow, and dyed gasoline suits fully as well as a highly refined product. Low sulfur was found to be an unnecessary requirement, particularly in warm climates. In many parts of the country the specification of one-tenth percent is entirely obsolete and it is only adhered to in some places because of the rigidity of state regulations. The only two useful ends which refining cracked gasoline serves are the production of motor fuel of good odor which will not form gum.

The unpleasant odor of some cracked gasolines is due to the presence of mercaptans. These may sometimes be largely removed by repeated washing with caustic soda, which forms mercaptides according to the equation

$$RSH + NaOH \rightarrow RSNa + H_2O \qquad (1)$$

Caustic soda will only remove the lower mercaptans and these only until it is partially saturated. For economy therefore, the caustic is regenerated, i.e., boiled to cause reversal of the reaction and liberation of the mercaptans in gaseous form. The caustic may then be reused for a number of cycles. After this treatment some gasolines are marketed, but usually further removal of mercaptans is brought about by what is known as sweetening. This is usually treatment with doctor solution (sodium plumbite) and sulfur. The reactions occurring are:

$$RSH + Na_2PbO_2 \rightarrow RS\ PbO\ Na + NaOH \qquad (2)$$
$$2RSH + Na_2PbO_2 \rightarrow (RS)_2Pb + 2NaOH \qquad (3)$$

On addition of sulfur polysulfide-lead compounds are first formed, following reactions (4) and (5):[1]

$$(RS)_2Pb + S \rightarrow RSS\text{-}Pb\text{-}SR \qquad (4)$$
$$(RS)_2Pb + 2S \rightarrow RSS\text{-}Pb\text{-}SSR \qquad (5)$$

These complexes break down according to reaction (6):

$$RSS\text{-}Pb\text{-}SR \rightarrow RSSR + PbS \qquad (6)$$

or if excess sulfur is used, probably according to reactions (7) and (8):

$$RSS\text{-}Pb\text{-}SR + S \rightarrow RSSSR + PbS \qquad (7)$$

$$RSS\text{-}Ph\text{-}SSR + S \rightarrow RSSSR + PbS \qquad (8)$$

When the doctor reaction goes as desired only reaction (6) occurs and the mercaptans are converted into disulfides. However, if an excess of sulfur is used, reactions (7) and (8) take place, and probably in any case, some trisulfides remain in the gasoline. The presence of polysulfides reduces the antiknock value of the gasoline and at least the higher polysulfides lessens the response of the gasoline to inhibitors. For this reason sweetening should be carried out with the least possible amount of sulfur and this is aided by efficient mixing of the reagents with the gasoline.

While the larger part of the gasoline of the country is sweetened with doctor solution a newer process employing copper salts is rapidly coming into wide spread use. In this process, the essential reactions are (8) and (9):

$$Cu^{++} + RSH \rightarrow RSSR + H^{+} + Cu^{+}$$

$$2Cu^{+} + 2H^{+} + O_2 \rightarrow H_2O + 2Cu^{++} \qquad (9)$$

The gasoline is first brought in contact with the copper salts, which oxidize the mercaptans to disulfides. Either at the same time or in a separate step the reagent is blown with air to reconvert the cuprous copper to the cupric form.

Prevention of gum formation in cracked gasoline has long been brought about by treatment with sulfuric acid or fullers earth. A more economical method of securing gum stability is the addition of an oxidation inhibitor, which prevents loss of hydrocarbons, saves the loss in antiknock value usually caused by chemical refining, the cost of reagents and of operating treating process. Much of the gasoline now sold is given no treatment beyond sweetening and adding inhibitor. Such gasoline often changes less in storage than motor fuel refined by other methods. Aminophenols, naphthols, and wood tar fractions are the most widely used commercial antioxidants. Their use is steadily increasing and probably will eventually largely replace other treating methods.

[1] Ott and Reid, Ind. Eng. Chem. *22*, 884 (1930).