THE RELATIONSHIP OF THE CHEMICAL STRUCTURE OF CUTTING OILS TO THEIR OXYGEN COMPATIBILITY

R. A. Walde Air Products and Chemicals, Inc. Allentown, Penn.

A considerable amount of work has been done in the past studying the compatible concentration of various oils with high pressure oxygen. This work has employed numerous types of test devices and has examined lubricating, compressor, and cutting oils. Compatible concentration has normally been described as the concentration of oil as a film below which no reaction takes place. Depending upon the type of oil and the test used, results ranging from a few mg./sq. ft. up to 500 mg./ sq. ft. have been reported as being the upper limit of the safe region. In most of these studies little attention was given to the effect of chemical structure on the compatibility of a particular series of oils.

It is the objective here to demonstrate the importance of considering chemical nature as well as concentration when establishing safe concentration levels for a particular series of oils. For this study one has chosen to examine cutting oils which are commonly used in the manufacture of machine parts such as valves. The oils were classified according to their chemical structure by infrared analysis and their compatible concentration determined in the presence of pure gaseous oxygen at 1,500 lb./sq. in. gauge.

Test system

The basic test system used was originally developed by E. Kehat of Air Products and Chemicals and is described in a paper that was presented at the Cryogenic Engineering Conference in August, 1961. Modifications have been made in the test procedure that give improved results. Figure 1 shows a schematic diagram of the test system. The main body is composed of a 2-it. piece of schedule 40 stainless steel pipe with a rupture disk at one end, a gas feed orifice at the other end, and a wire igniter placed in the center. The effective surface area is 0.689 sq. ft.

The oil films are placed on the surface of the bomb by adding a particular volume of a methylene chloride solution of the oil to the bomb and evaporating the solvent while rotating in a hot water bath. The concentration in mg./sq. ft. is determined by the concentration of oil in the methylene chloride solution and the volume of it added to the bomb. It is important during evaporation to be sure that all of the solvent is completely removed since small quantities of residual solvent can have a considerable effect on the results obtained. Methylene chloride is a very good solvent for this purpose because of its volatility and low reactivity with oxygen.

Effect of oil film

A significant test variable observed in this study was the effect that an oil film placed on the igniter wire during evaporation had on the compatible concentration. Table 1 gives some comparative results of nonreactive concentrations determined for hexadecane and cutting

+Reaction still occurs.

oil blends when the igniter wire was in place during evaporation of the solvent and when it was put in place after evaporation of the solvent. As can be seen, the nonreactive concentrations determined are much lower when the igniter wire is free of any oil film than when it is coated with oil. These lower concentrations are possibly due to ablative cooling of the igniter wire by the oil film which results in a lowering of the initiation energy peak. In order to obtain meaningful results which can be uniformly correlated, the ignition system should not be contaminated with the oil. Therefore, in this study the ignition system was put in place after evaporation of the solvent had been completed. After evaporation of the solvent and putting the ignition system in place, the bomb was purged with oxygen, pres surized to 1,500 lb./sq. in. gauge, and the wire ignited. The ignition system used was composed of a 1.75-in. piece of 11.5 mil Nichrome wire having a resistance of

Figure 1. Oil film oxygen compatibility apparatus.

0.7 ohms/ft. which was soldered to two electrode leads. The wire was flashed by passing 20 amp. of electricity at 7.7 v. through it.

Classification of cutting oils

For this study 20 types of commercial cutting oils were obtained from various vendors. Their infrared spectra were measured in chloroform solution and the oils were classified according to the types of chemical functionality observed. Based on similarities in infrared spectra the oils were placed into four classes. Table 2 shows these classifications and indicates the various types of functional groups observed

TABLE 2. CLASSIFICATION OF CUTTING OILS BY INFRARED SPECTRA.

Group	Principal groups by infrared spectra	Base type
	$C-H$, $C=0$, $C-O-C$	Ester
$_{\rm II}$	$CH-CH9$, $CH3$	Hydrocarbon
Ш	OH. CH. $C = 0$, $C - 0 - C$	Ester, alcohol
ŢV	OH. CH. $C = 0$	Acid salt
	OH complexed	water soluble

for the oils in each class. Group 1 shows very strong carbonyl and C-0-C absorption and was identified as ester base cutting oils. Group 2 shows only CH, $CH₂$, and CH₃ absorption bands and was identified as hydrocarbon base cutting oils. As can be seen, the majority of the oils studied fall into this group. Group 3 was similar to Group 2 but showed a strong OH band and was classified as being ester-alcohol base cutting oils. Group 4 showed strong OH and carbonyl absorption and these oils were found to be water soluble. They were given the classification of acid-salt-water soluble type cutting oils. Composite blends were prepared for each of these groups by mixing equal quantities of each oil in each group. This was done to minimize the number of samples that would have to be tested and was justified on the basis that the main variation between the oils in each group was viscosity or molecular weight.

Compatibility studies

Using these four composite blends of cutting oils, compatibility studies were carried out at various concentration levels. In each case the initial level chosen was such that violent reactions were obtained. The concentration of oil was lowered by increments of 50 mg./ sq. ft. until a nonreactive level was reached. Reaction was observed based on noise, pressure increase, evolution of heat, and odor within the bomb. Heat evolution was determined by feeling the bomb immediately after ignition. These reactions varied from loud detonations which broke the rupture disk to very mild reactions being determined only by the evolution of heat and the formation of odor. The nonreactive level was determined as that concentration at which no noticeable heat or odor was evolved upon examination of the bomb immediately after ignition. Table 3 shows the actual results for each of the four groups of oil.

TABLE 3. CUTTING OIL OXYGEN COMPATIBILITY CONCENTRATIONS.

Group	Chemical type	Nonreactive concentration, concentration, mg./sq.ft.	Increment of mg./sq.ft.
Ţ	Ester base	300	50
H	Hydrocarbon base	7	7
Ш	Alcohol ester base	150	50
TV	Water soluble acid		
	salt base	300	50
	Hexadecane	150	50
	Ester-type com-		
	pressor oil	200	50
	Hydrocarbon-type compressor oil	15	15

Nonreactive or compatible concentration is that concentration of oil in mg./ sq. ft. which is one increment below the next highest level at which reaction was observed to take place. For instance, in Group 1, the ester base-type cutting oils, reaction was observed to take place at 350 mg./sq. ft., but not at 300 mg./sq. ft. In Group 2, the hydrocarbon base cutting oils, reaction

took place at 14 mg./sq. ft., but not at 7 mg./sq. ft. For the ester base cutting oils, reaction took place at 200 mg./sq. it. but not at 150 mg./sq. ft. For Croup 4, the water soluble cutting oils, reaction took place at 350 mg./sq. ft., but not at 300 mg./sq. ft. For comparison several other oils are listed on this table. They are hexadecane and two commonly used hydrocarbon and ester type compressor oils.

Variation in safe concentration

These results show a considerable variation in the safe concentration level with chemical structure. The ester base and water soluble cutting oils are the most stable and the hydrocarbon base the least stable. These results demonstrate that oils containing oxygen and phosphorus atoms are more stable than straight hydrocarbon oils. The effect of branching on reactivity is observed by comparing hexadecane and the hydrocarbon base cutting oil. The hydrocarbon base cutting oil is highly branched and contains a number of tertiary hydrogen atoms, whereas the hexadecane is straight chain and contains none of these reactive sites.

These results amply demonstrate the importance of considering chemical nature when establishing safe concentration limits for oils. If a general specification

is to be established, the level must be set for the most reactive type in the group. In the case of cutting oils, it would be 7 mg./sq. ft. On the other hand, if the specification is set such that all parts are machined using an ester base cutting oil, a much higher safe contamination level can be established, in this case 300 mg./sq. ft. Any test system which is designed to determine oil concentration on a pipe or valve should also take into account the chemical nature of the oil. In this regard, one would measure the oxidizability of the system as determined by both chemical nature and concentration.

Acknowledgment

The author wishes to acknowledge the help of M. K. Brophy, who assisted in carrying out these experiments.

This work is a continuation of work by Air Products and Chemicals presented in Volume 4 of Safety in air and ammonia plants, "Hazard Level of Hydrocarbon Films in Oxygen Systems," by W. L. Ball.