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An Attempt to Develop a New Fire-Resistant Hydraulic Fluid Based on Water-in-Oil Microemulsions

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ABSTRACT

The strategy for the development of microemulsion-based fire-resistant hydraulic fluids has been expounded. Phase diagrams were constructed for mixtures of water, oil and nonionic surfactants with and without cosurfactants. From these phase diagrams the boundaries of the monophasic area were outlined. After the major components had thus been determined, several preliminary formulations were developed by incorporating suitable additives into the oleic ingredient of the hydraulic fluid. These carefully chosen additives improve considerably the performance of the hydraulic fluid. The resulting microemulsion-based compositions complied with most of the requirements set for fire-resistant hydraulic fluids.

Model systems pertinent to such formulations were utilized in order to investigate structural factors, which induce enhanced water solubilization. The role played by alcohols in this context was elucidated in terms of an empirical equation. Sophisticated scattering and NMR methods have demonstrated the variations in the microstructure of a high water content model system. Sub-zero differential scanning calorimetry (DSC) techniques have revealed the existence of two types of water (free and bound) and determined their relative concentrations.

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RESUMO

A técnica de desenvolvimento de flüidos hidráulicos não-inflamáveis foi descrita. Foram construidos diagramas de fase para misturas de água, óleo e surfatantes com e sem cosurfatantes e a região monofásica foi bem definida. Subsequentemente, foram preparadas formulações preliminares incorporando aditivos adequados na fase oleosa do flüido hidráulico. As composições, baseadas em microemulsões, satisfazeram amaioria dos prerequisitos de flüidos hidráulicos não-inflamáveis. As interações no meio e particularmente a função dos álcoois e da água foi estudada usando técnicas de espalhamento de raios-X à ângulo baixo (SAXS), calorimetria diferencial de varredura (DSC) e ressonância magnética nuclear (RMN). Foi demonstrada a existência de dois tipos de água (livre e ligada) e foi determinada a concentração relativa.

INTRODUCTION

In principle, almost every liquid may function as a hydraulic fluid. However, because of its obvious economic and environmental advantages water was normally used for transmission of power[1]. The advent of high-performance pumps has introduced the use of mineral oils. These hydraulic fluids have been improved by refining the mineral oil and incorporating adequate additives. The Achilles heel of mineral oil-based hydraulic fluid is its high flammability, which may, in some important applications, almost nullify its numerous advantages. Such hydraulic fluids have already caused many disasters in both civilian and military applications. The risk of fire will be more pronounced in future applications since much higher pressures are planned to be applied[2]. The historical evolution of hydraulic fluids and the present situation are described in the following scheme:

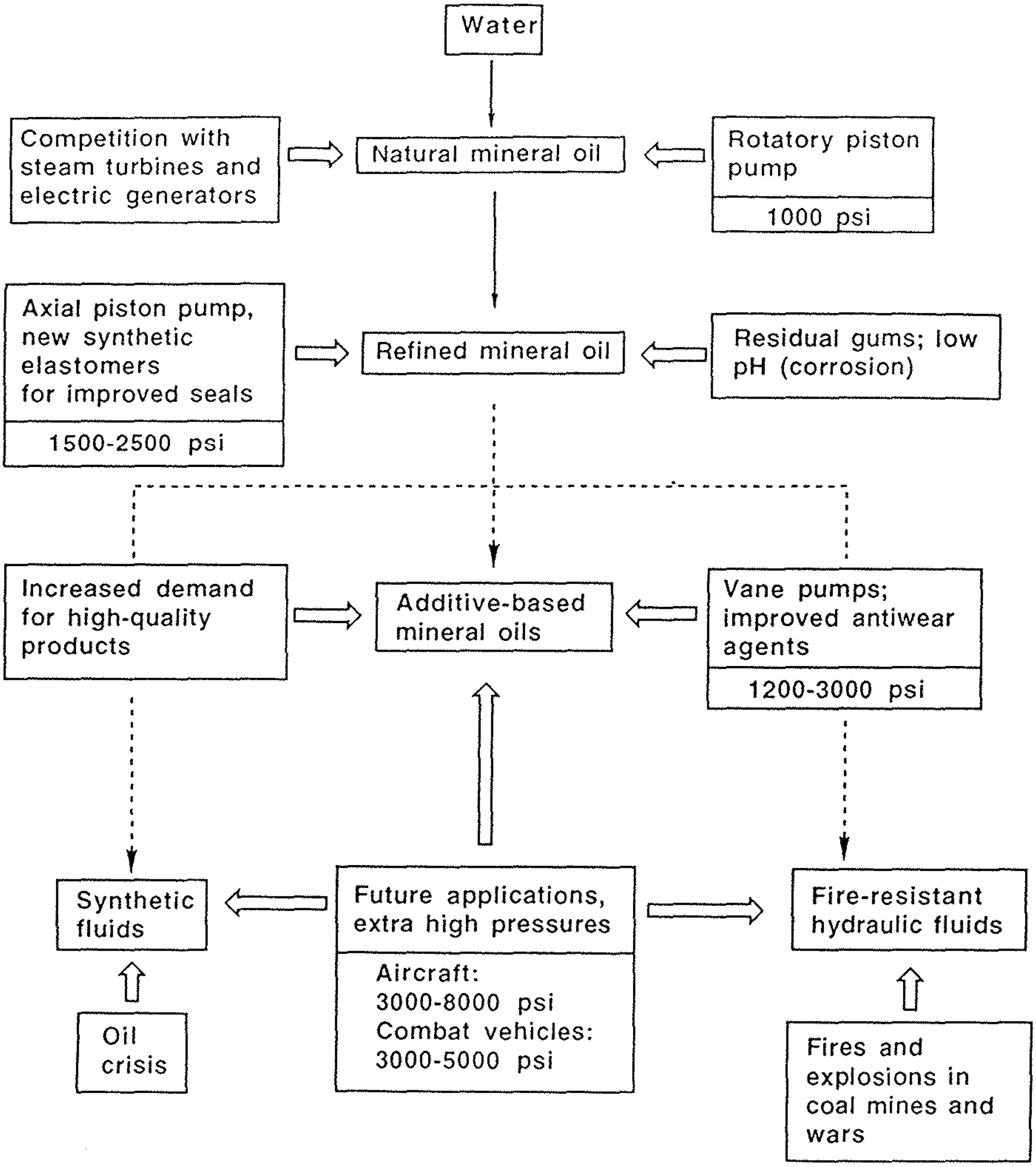

Fig. 1: The historical evolution of hydraulic fluids.

Most suggested fire-resistant hydraulic fluids may be classified[3] in one of the four groups: HFA, HFB, HFC and HFD (see Table 1).

TABLE 1: Classification of fire-resistant hydraulic fluid.

Classification	Description
HFA	High water-based fluids which are further divided into:
HFA-E	Oil-in-water emulsions or aqueous solutions containing max. 20 mass % of combustible materials.
HFA-S	Solutions of chemicals in water containing min. 80 mass % water.
HFB	Water-in-oil emulsions containing max. 60 mass % of combustible materials. Water content normally 40-45 mass %.
HFC	Aqueous solutions with viscosity-increasing (polymeric) additives or water-glycol solutions. Usually contained min. 35 mass % water.
HFD	Fire-resistant nonaqueous fluids such as phosphate esters (most common), halogen-containing compounds, etc.

Each type has its pros and cons. The main disadvantage of the four types will now be described in a nutshell. HFA suffers from almost all the drawbacks of water, such as rust, poor lubricity and wear resistance[4], limited range of operating temperatures[5] and microbial infestation[6]. HFB fares no better, as like any other emulsion, it is inherently unstable[1]. HFC suffers from poor lubricity[7] and incompatibility with some metals and sealants[8]. HFD is expensive[8], too heavy for certain applications and suffers from incompatibility with construction materials and additives[2].

In our case, the hydraulic fluid could not have had density higher than 0.95-1.00 g/cc as this fluid was designed to operate in a given system. Our research strategy was based on the following principles:

Of all the possibilities suggested for fire-resistant hydraulic fluids, most promising seems to be a combination of the excellent hydraulic qualities (especially lubricity) of mineral oil with the fire-resistance and environmental advantages of water. This rules out the HFC and HFD types.

There should be an optimal balance between the fire-resistance (maximum water content) and the hydraulic qualities (maximum mineral oil content) of the hydraulic fluid. Excess of either water or oil will be detrimental to the product. This principle rules out the HFA type.

The remaining type, HFB, suffers from instability, and our solution to this is to use microemulsions instead of emulsions. The idea of using microemulsions as hydraulic fluids is quite recent and does not appear often in the relevant technical literature (scientific articles and patents). A microemulsion is a clear and thermodynamically stable mixture of water, oil and suitable amphiphiles (substances that due to their unique molecular structure can hold water and oil together). Microemulsions are much easier to prepare than ordinary emulsions, as they form spontaneously[9]. They are stable under a wide range of operating conditions[10] and in storage, have high solubilization capacity for both oil and water[11], and provide better protection than simple emulsions against corrosion and wear[12]. They are also easier to filter[13] and are less volatile. Thus, microemulsions may be a most promising solution to the problem of fire-resistant hydraulic fluids. In the future, we will be able to replace the mineral oils by more sophisiticated and efficient synthetic fluids and hopefully to microemulsify them.

EXPERIMENTAL PROCEDURE

Materials

In all formulations the oleic phase was based on a paraffinic mineral oil (produced by Paz Oil Co., Ltd., Israel) consisting of ca. 70% paraffinic oil and 30% naphtenic and aromatic fractions. The surfactants used were polyoxyethylene (2) oleylalcohol (known also as $C_{18:1}(EO)_2$ or Brij 92), polyoxyethylene (20)-oleylalcohol (knowl also as $C_{18:1}(EO)_{20}$ or Brij 98), both purchased from ICI Specialty Chemicals, Germany, and 2-ethylhexylsulfosuccinate sodium salt (known also as AOT) from American Cyanamid Company, USA. 1-pentanol (Aldrich Chemical Co., Inc., USA) was used in some experiments as a cosurfactant. Distilled water was used as the aqueous phase. Alkylbenzotriazole, ethoxylated alkanolamide, tetraethylene glycol, zinc dialkyldithiophosphate (ZDDP), a nitroalkylmorpholine derivative and 1-phenyl dodecane, all obtained from Paz Oil Co., Ltd., Israel, were used as additives in various formulations as will be described in the text. For the model systems, n-dodecane (sometimes also n-decane, n-tetradecane and n-hexadecane) from Aldrich Chemical Company, Inc., USA (purity ca. 99%) was used as the oleic phase. The surfactants used were polyoxyethylene (10) oleylalcohol (known also as $C_{18:1}(EO)_{10}$ or Brij 97), polyoxyethylene (10) stearylalcohol (known also as $C_{18}(EO)_{10}$ or Brij 76) of ICI Specialty Chemicals, Germany, and highly purified octaethylene glycol mono-n-dodecylether [$C_{12}(EO)_8$] from Nikko Chemicals Co., Japan; 1-pentanol was one of the main cosurfactants, but sometimes other n-aliphatic alcohols (such as 1-butanol, 1-hexanol, etc.) were also used. All of them were purchased from Aldrich Chemical Company, Inc., USA. Water for the model systems was double distilled.

Determination of the phase diagrams

The phase behavior of the three-component systems was depicted on ternary phase diagrams. These diagrams are outlined on triangles. Each corner of such a triangle represents 100% of the component whose name appears near that corner. The behavior of four-component systems is described on a pseudo-ternary phase diagram in which the weight ratio of two components was fixed. Usually, the alcohol:oil weight ratio was held constant at 1:1. The construction of the phase diagram was conducted in a thermostatic bath at a given temperature in the following way. Mixtures of surfactant, alcohol (cosurfactant) and oil were prepared in culture tubes sealed with viton-lined screw caps at predetrmined weight ratios of (alcohol + oil) to surfactant of 9:1, 8:2, . . . 1:9, 0.5:9.5 (10 samples in all). To these mixtures small weighed amounts of water were added dropwise at first and then larger aliquots such that the weight fraction of each water increment was at least 0.02. These aqueous mixtures are samples along water dilution lines drawn to the water apex from the opposite side of the triangle. In all the samples tested, evaporative loss was negligible. Nearly all samples were equilibrated during a time interval which varied from a few minutes to 24 hours. The tubes were then inspected visually. Optical birefringence (observed between crossed polarizers) and apparent increased viscosity indicated the presence of a liquid crystalline phase. Identification of the liquid crystals was done by small angle X-ray scattering (SAXS). Appearance of turbidity was considered as an indication for phase separation. In some doubtful cases, the samples were let to settle and give clear phases. The phase behavior of such samples was determined only after sharp interfaces have become visible. The completion of this process was hastened by centrifuging the samples. Every sample which remained transparent and homogeneous after vigorous vortexing was considered as belonging to a monophasic area in the phase diagram. In this way we were able to outline the phase diagram of the system.

RESULTS AND DISCUSSION

$C_{18:1}(EO)_2$ and $C_{18:1}(EO)_{20}$ systems

Figure 2 is a tricomponent phase diagram of $C_{18:1}(EO)_2$/mineral oil/water at two different temperatures The surfactant is too hydrophobic (HLB 4.9) to solubilize appreciable amount of water, even in the presence of high concentrations of surfactant. The L_2 phase represents reverse micelles swollen by the water solubilized in their core. Quasielastic light scattering (QLS) measurements seem to show that the aggregates are few and very small. The area of the L_2 phase is narrow and practically unaffected by the temperature. This is understandable as the temperature effect on the very short EO chains is quite limited.

Figure 3 is the phase diagram of the system $C_{18:1}(EO)_{20}$/mineral oil/water at two different temperatures. This surfactant is hydrophilic (HLB 15.3), has only minor solubility in oil but increased solubility in water. However, geometrical considerations suggest that L_2 will still be rather small though the amount of solubilized water (ca. 10 wt%) is larger than that in the case of the $C_{18:1}(EO)_2$ system. QLS measurements indicate the presence of small aggregates in the L_2 region. In addition, a large area of liquid crystalline phase is seen (region E in Fig. 3). Optical microscopy and SAXS measurements have proved the hexagonal nature of this phase. This is in good agreement with statements[14] that nonionic surfactants containing long hydrophilic chains tend to strongly hydrate the water and therefore transform into a hexagonal structure. The variation of temperature from 25°C to 45°C did not significantly affect the phase diagram.

Figure 4 is the phase diagram of the system $C_{18:1}(EO)_2$ + $C_{18:1}(EO)_{20}$ at 0.42:0.58 (wt/wt), respectively/mineral oil/water (HLB 10.9). This ratio between the surfactants was selected because it represents the required HLB of the paraffinic oil used in these experiments. The required HLB is the optimal HLB for the preparation of O/W macroemulsions in which the oil phase was a similar paraffinic oil.

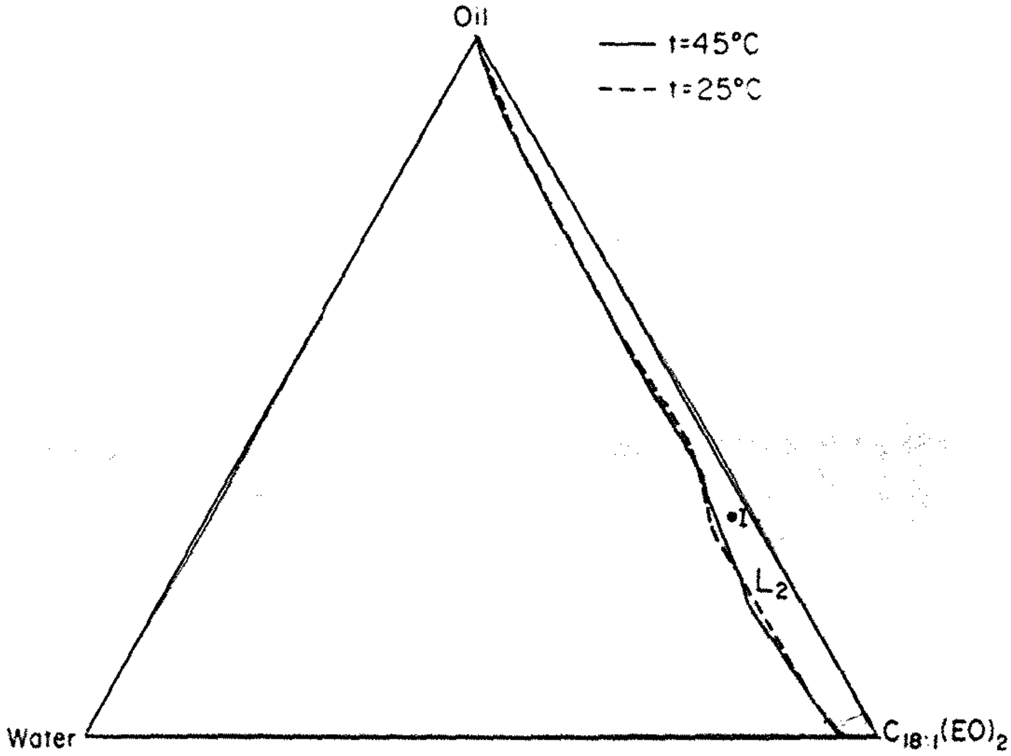

Fig. 2: Phase diagram of the system $C_{18:1}(EO)_2$/mineral oil/water.

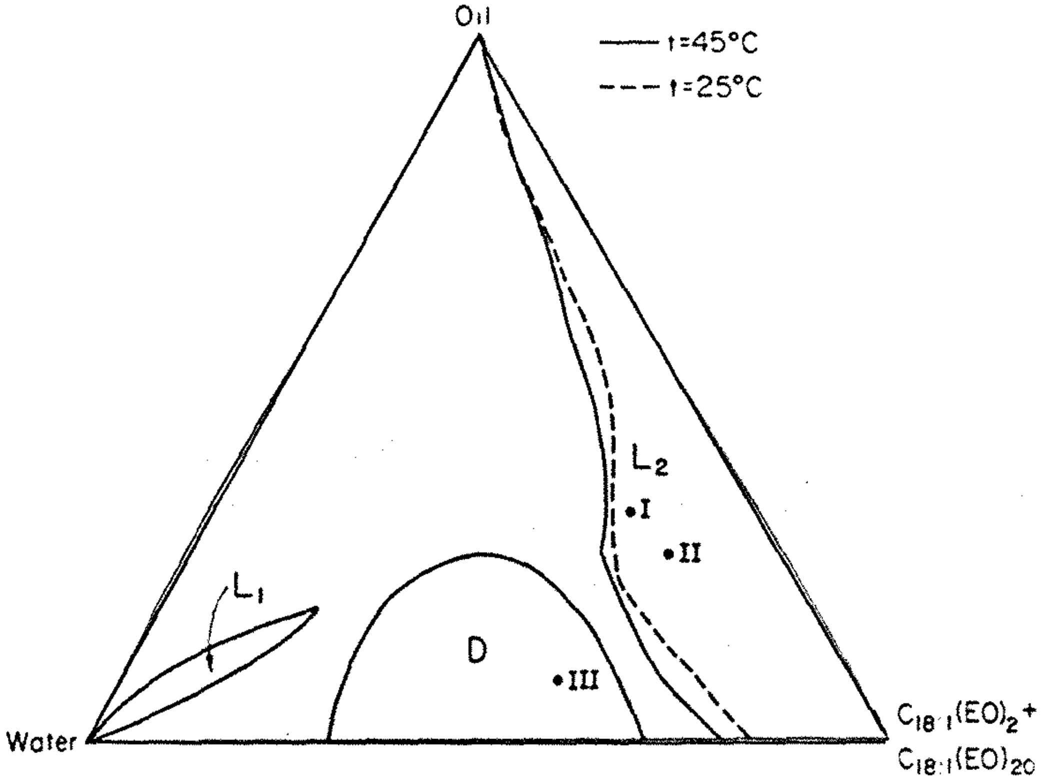

Fig. 3 Phase diagram of the system $C_{18:1}(EO)_{20}$/mineral oil/water.

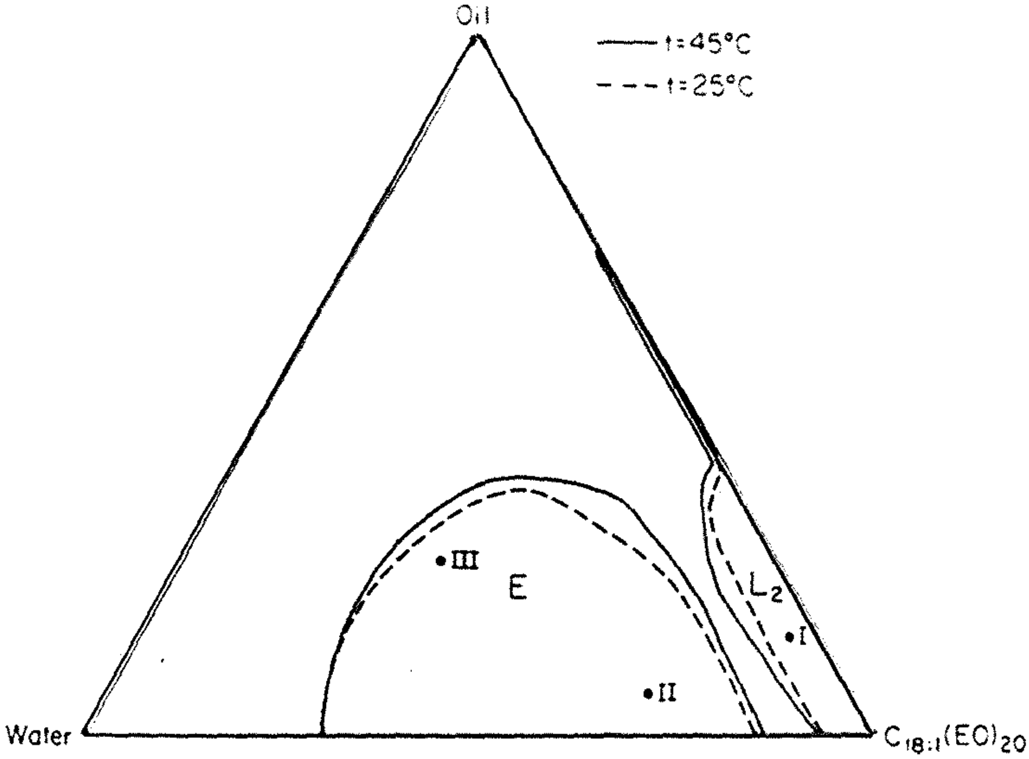

Fig. 4: Phase diagram of the system $C_{18:1}(EO)_2$+$C_{18:1}(EO)_{20}$ [0.42:0.58 (wt/wt)]/mineral oil/water.

The synergism between the two surfactants is expressed in the amount of solubilized water, which is larger than in the case of $C_{18:1}(EO)_2$ and $C_{18:1}(EO)_{20}$ operating separately. The L_2 phase is relatively larger and 22 wt% water may be solubilized. In addition, a small L_1 phase is detected. The L_1 phase consists of swollen regular micelles in which small amounts of oil have been solubilized. Between the L_1 and L_2 regions of the phase diagram, a liquid crystalline phase is also well defined. This mesophase was identified as lamellar. Table 2 compares the results of these three systems.

TABLE 2: Factors for quantitative evaluation of the surfactants relative efficiency for solubilizing water. system: Mineral oil/surfactant/water.

	$C_{18:1}(EO)_2$		$C_{18:1}(EO)_{20}$		$C_{18:1}(EO)_2$/ $C_{18:1}(EO)_{20}$ (0.42/0.58)	
TEMPERATURE (°C)	25	45	25	45	25	45
Water solubilization (max. wt%)	6.3	7.3	6.3	8.7	22.1	23.4
Surfactant content at max. water solubilization (wt%)	68.9	80.1	72.9	79.0	60.9	67.1
Water/surfactant weight ratio at max. solubilization	0.09	0.09	0.09	0.11	0.36	0.35
L_2 area fraction (%)	5.3	6.1	2.7	6.9	17.0	21.8

Stability of additives-containing microemulsions

Preparing a stable microemulsion that functions as a hydraulic fluid is not a simple task. It is accomplished by judiciously assimilating suitable additives in the oil, or sometimes also in the aqueous phase. The selection of an inappropriate additive may, however, cause the breakdown of the microemulsion, especially in the case of water-rich formulations or when the microemulsion is subjected to relatively high and low temperatures. The resulting two phases have a detrimental effect on the hydraulic system: the oil is highly flammable and the water, while able to douse any fire in the oil, may lead to severe corrosion and wear problems. Thus, although the preparation of a microemulsion per-se is not necessarily difficult, the adaptation of a microemulsion for a specific application, such as the preparation of a fire-resistant hydraulic fluid, is far from being straightforward. We will illustrate our way of attacking this problem on three selected compositions shown in Table 3. For proprietary reasons we obviously cannot demonstrate here our more advanced formulations.

TABLE 3: Compositions of three selected formulations derived from phase diagram presented in Fig. 4.

Formulation	Composition in wt%			
	Water	Oil	$C_{18:1}(EO)_2$	$C_{18:1}(EO)_{20}$
1	8.8	49.8	17.4	24.0
2	13.8	25.7	25.4	35.0
3	83.7	5.2	4.7	6.4

Formulations 1 and 2 correspond to the L_2 region and formulation 3 corresponds to the L_1 region of the phase diagram. In each formulation six additives were incorporated during the preparation step. The list of these additives, together with their function and their recommended concentration range, is shown in Table 4.

TABLE 4: Selected additives for improving physical, chemical, rheological and tribological properties of hydraulic fluids.

	Additive name	Functional application	Recommended concentration range (wt%)
1	Alkylbenzotriazole	Copper passivator	0.1-1.0
2	Ethoxylated ethanolamide	Corrosion inhibitor	0.1-1.0
3	Tetraethylene glycol	Anti-foam and pour-point depressant	0.1-1.0
4	ZDDP*	Antiwear agent	0.1-1.0
5	Nitroalkylmorpholine derivative**	Biocide	0.001-2.0
6	1-Phenyldodecane	Anti-swelling agent	0.001-0.2

*Zinc dialkyldithiophosphate.
**This additive consists of a mixture of 4-(2-nitrobutyl)morpholine and 4,4'-(2-ethyl-2-nitrotrimethylene)dimorpholine.

The additives were consecutively added, each at its minimum level, without destabilizing the microemulsion. We have also determined the additive dissolution capacity of our system. This parameter is defined as the maximum concentration of each additive that could be introduced into the microemulsion without destabilizing it, measured in the absence of other additives. Thus, it enables us to estimate the mutual compatibility of the additives as well as the stability of the system additives + microemulsion (see Table 5).

TABLE 5: Microemulsion dissolution capacity for each additive incorporated individually in the three selected formulations.

Additive name	Maximum capacity (wt%)		
	Formulation 1	Formulation 2	Formulation 3
Alkylbenzotriazole	26.0	27.1	0.1
Ethoxylated alkanol-amide	27.0	26.7	0
Tetraethylene glycol	27.0	7.8	0.3
ZDDP	26.0	26.3	0
Nitroalkylmorpholine derivative	25.7	27.2	0.5
1-Phenyldodecane	27.0	27.5	0

It is clearly seen that the dissolution capacity of Formulation 3 for all the additives tested is low, while Formulations 1 and 2 may be infused with the same additives at levels well above their minimum required concentration. Formulation 2 was selected for performance evaluation since it seemed to be more stable in the long range stability tests than Formulation 1, which has quite similar dissolution capacity for these additives. The final composition of Formulation 2 is given in Table 6.

TABLE 6: Final composition of microemulsion prepared for performance testing.

Component	wt%
Mineral oil	24.6
$C_{18:1}(EO)_2$	24.0
$C_{18:1}(EO)_{20}$	33.3
Water	13.3
Additives:	
ZDDP	2.5
Ethoxylated alkanolamide	0.5
Alkylbenzotriazole	0.5
Tetraethylene glycol	0.1
Nitroalkylmorpholine derivative	1.0
1-Phenyldodecane	0.2

Hydraulic fluids have to undergo a long series of chemical, physical, rheological and tribological tests, according to stringent specifications. Preliminary tests done on Formulation 2 have shown it to be stable for more than two years. It has good anti-wear protection (four-ball test) and it complies with the foaming characteristics required by Military Specification MIL-H-46170 B (1982). However, the most obvious flaw in this preliminary formulation is its low water content.

Improvement of water solubilization by addition of alcohol

In order to enhance water solubilization in the L_2 phase, the oil component in the phase diagram was replaced by 1:1 (wt/wt) mixture of the same oil with pentanol. Fig. 5 shows clearly that the addition of pentanol improved the water solubilization of the system. A similar but more pronounced effect was demonstrated (see Fig. 6) for the system $C_{18:1}(EO)_{10}$/dodecane/pentanol/water, where the weight ratio dodecane:pentanol was held constant at 1:1. This has led

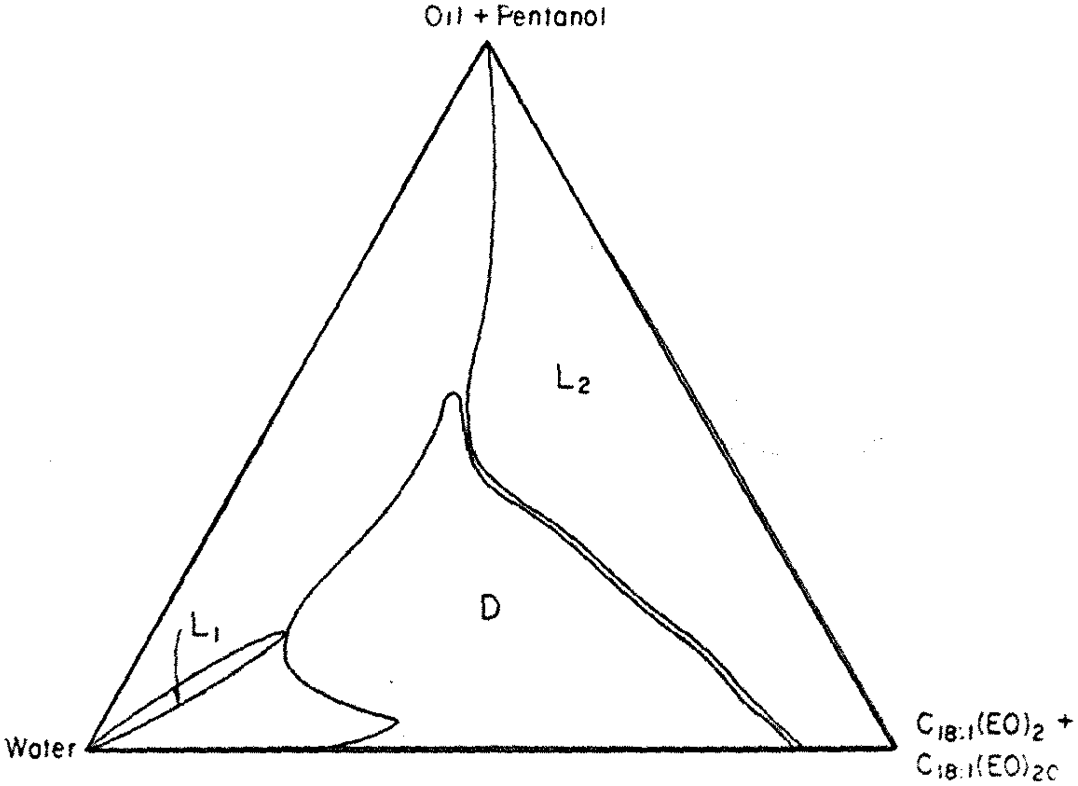

Fig. 5: Phase diagram of the system $C_{18:1}(EO)_2$+$C_{18:1}(EO)_{20}$ [0.42:0.58 (wt/wt)]/mineral oil + pentanol [1:1 (wt/wt)]/water.

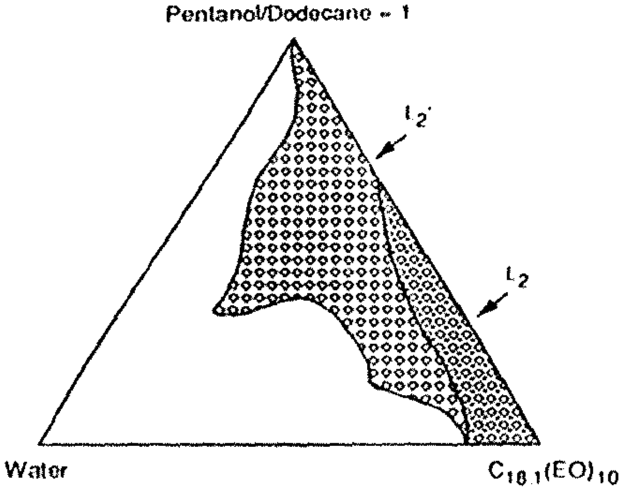

Fig. 6: Phase diagram of the system $C_{18:1}(EO)_{10}$/dodecane/pentanol/water; weight ratio dodecane:pentanol is 1:1.

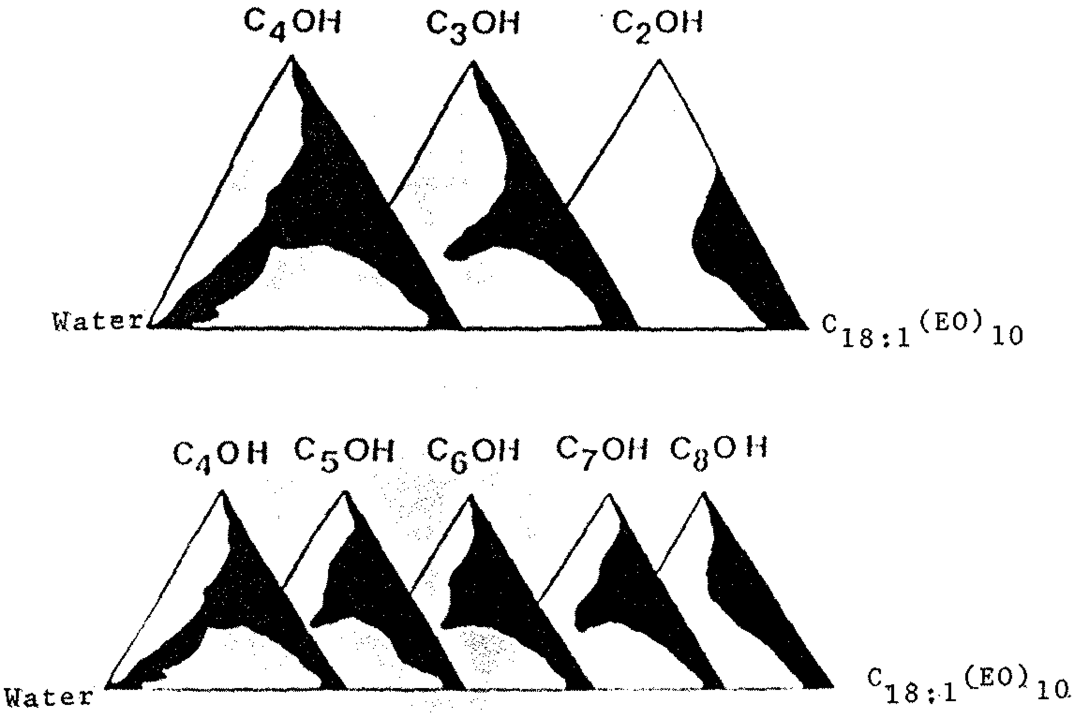

Fig. 7: Variation of water solubilization with the alcohol chain length (N_A) for the system $C_{18:1}(EO)_{10}$/dodecane/n-aliphatic alcohol/water.

us to systematically investigate the effect of a series of n-aliphatic alcohols on water solubilization. Naturally, in the presence of all the additives needed for adequate functioning of hydraulic fluid, such a systematic study is not feasible and a model system with rather similar major constituents is used here instead. The multi-component mineral oil was replaced by the pure hydrocarbon n-dodecane and the nonionic surfactant $C_{18:1}(EO)_{10}$ was substituted for the less effective binary mixture of the surfactants $C_{18:1}(EO)_2$+$C_{18:1}(EO)_{20}$. Thus, the model system tested was $C_{18:1}(EO)_{10}$/dodecane/n-aliphatic alcohol/water. The weight ratio dodecane:alcohol was fixed at 1:1. The results are shown in Fig. 7. It is evident that the water solubilization capacity is sensitive to the alcohol chain length (N_A) and moreover, passes through a maximum at a certain N_A. For anionic microemulsions it was shown[16] that the maximum amount of water, which may be solubilized, is reached when the oil chain length, N_o, plus that of the cosurfactant, N_A, is equal to the surfactant chain length, N_s, i.e. $N_o + N_A = N_s$. This BSO (Bansal, Shah, O'Connell) equation was examined by us for the first time in relation to nonionic surfactants. Our analysis, which elucidates the conditions for which this equation is obeyed, may assist in optimization of nonionic microemulsion systems (Garti, N., Aserin, A., Ezrahi, S. and Wachtel, E., accepted).

Investigation of the microstructure of a model system

The improvement of the preliminary microemulsion-based formulations of fire-resistant hydraulic fluid is a complicated task. It may be benefited by the intensive study of the variations in the microstructure of a similar model system. The system chosen is composed of $C_{12}(EO)_8$/dodecane/pentanol/water [dodecane:pentanol=1:1 (wt/wt)]. These variations may *prima facie* have only a theoretical significance, as they are not visualized on a macroscopic scale. However, we may take advantage of them for our purpose. Our model system contains more than 85 wt% water, but it is obvious that the amount of water, which may be solubilized in the inner phase of the microemulsion, is limited. Thus, an inversion from a water-in-oil (W/O) to an oil-in-water (O/W) microemulsion has necessarily occurred. When water constitutes the outer phase of the microemulsion, the system is prone to the drawbacks typical of water, such as rust, poor lubricity, pump cavitation, microbial intrusion, etc. Evidently, it is necessary to locate the region of this inversion in the phase diagram. Another significant point is the distinction between bound and free water. The free water is similar in their properties to bulk water, while the bound water (which is associated with surfactant molecules) has quite different properties. From an operational point of view it is important that bound water evaporates slower than free water[17].

The inversion region was determined by nuclear magnetic resonance (NMR) methods (D. Waysbort et al., submitted) and differential scanning calorimetry (DSC) techniques (N. Garti et al., in preparation). DSC was also used to evaluate the distribution of free and bound water in the model system. On the basis of our experimental data the monophasic area in the phase diagram may roughly be divided into three regions: the water poor- and water rich- regions and an intermediate region connecting them. The shape and size of the surfactant aggregates, which prevail in these regions, have been determined using scattering methods and direct imaging by transmission electron microscopy (N. Garti et al., in preparation).

CONCLUSIONS

- The conception of preparing fire-resistant hydraulic fluids on the basis of nonionic microemulsions has been proved.
- Such microemulsions were obtained by preparing phase diagrams of the major components (water, oil, surfactants and cosurfactants). Inspection of the single-phase region of the phase diagrams has led us to the selection of adequate compositions into which effective additives were incorporated.

These preliminary formulations were examined by standard test methods and the results seem to be very promising.

The most pronounced drawback of the preliminary formulations was their rather low water content. It has been shown that pentanol (as well as other alcohols and other types of cosurfactants, which cannot obviously be described here) increases water solubilization in these systems.

The BSO equation, which has formerly been applied to anionic microemulsions was shown by us to be also valid for nonionic systems.

The investigation of a suitable model system may yield useful information about the desired formulations too. The microstructure of such a model system has profoundly been investigated, using advanced spectroscopic calorimetric and microscopic techniques. The results of this investigation have shown the variation of the structure with the water concentration, and located the region in which the inversion from water-in-oil to oil-in-water microemulsion had occurred.

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