EXPERIMENTAL OIL WEATHERING STUDIES IN HYDRAULIC CANAL AND OPEN POOL TO PREDICT OILS BEHAVIOR IN CASE OF CASUAL SPILLAGE

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ABSTRACT: *When spilled at sea, a crude oil is subjected to weathering processes such as evaporation, emulsification, dispersion and photooxidation, which occur under the influence of natural conditions. According to its weathering stage, the oil is continuously changing in terms of chemical composition and physical properties. Understanding and predicting these transformations is a key element in evaluating the potential impacts, optimizing response options and implementing the emergency response plan to spillage.*

The objective of this study was to get experimental data on the behavior of crude oils from different oil fields. The various weathering processes were simulated realistically in CEDRE's hydraulic canal, in which different marine water conditions can be recreated: wind, waves, and UV light. All the experiments were carried out with the same agitation level and at two temperatures, 10 and 20°C. Six different oils were tested and the different parameters measured or assessed were: density, viscosity, water content and kinetics of emulsification, chemical composition and kinetics of evaporation, flash point, emulsion stability, oil adhesion, and chemical dispersibility. The evolutions proved to vary considerably according to the nature of the oil, the temperature and the photooxidation process.

The weathering of one crude was also assessed outside in a large pool to provide a calibration of the evaporation and emulsification kinetics in realistic conditions compared to the flume test. The canal speeds up these processes by a factor between 4 and 6.

Introduction

Oil spilled at sea is subjected to a range of environmental effects. Small and light molecules evaporate, especially in windy conditions, some compounds dissolve into the water column, most of the aromatic compounds are liable to be photochemically oxidized, some oil can be dispersed, either naturally or following the application of dispersants, while the oil remaining on the water surface can be emulsified with sea water. According to its weathering stage, the state of the oil is continuously changing in terms of chemical composition and physical properties. Oil can get increasingly viscous and become a new persistent pollutant in the environment. The behavior of the weathered oil is often different from that of the original one. Understanding these changes is a key element in evaluating the potential impacts and optimizing the emergency response to an oil spill. Each spill entails a series of questions in terms of physical-chemical evolutions of the oil and choice of response techniques that are associated with.

The objective of this study was to obtain experimental data on the behavior of crudes from different oil fields. These data will be used by people in charge of preparing and implementing the emergency response plan to an oil spill. In addition, when a large panel of products has been weathered in the flume with similar energy conditions and at a minimum of two temperatures, the resulting data will provide a useful basis for predicting the behavior of an oil according to its initial chemical composition and physical parameters. Finally, the evolution of one oil in an open pool was monitored during 3 days to provide a calibration of the flume in real conditions.

Experimental weathering

The weathering of crude oils is complex, as different processes (evaporation, dispersion, emulsification, photooxidation) take place simultaneously (Ducreux *et al.*, 1986). However, no laboratory method exists to consider all the parameters simultaneously and to simulate the whole weathering process.

To simulate these various phenomena realistically, CEDRE has equipped its facilities with a hydraulic canal in which different marine (as well as inland) water conditions can be re-created, such as wind, waves, UV light and, if necessary, dilution (Guyomarc'h *et al.*, 1999a). With this equipment, it is possible to weather samples of a specific oil under a variety of climatic conditions. In this study, all the experiments were carried out with the same agitation level and at two temperatures (10 and 20°C).

In addition, an other experimental device was used to study the weathering and dispersibility of various oils in "real" conditions. Six mesocosms were set in a harbor and the evolution of one oil was monitored in each of them, thus providing replicates. Only the weathering study will be presented and the repeatability of the evolutions will be discussed.

Flume test weathering

CEDRE has studied the weathering of samples from different oil fields in its hydraulic canal (Figure 1) for 7 days to determine the fate and behavior of these oils in the first hours and days after an oil spill. During the test, the following parameters were assessed:

- Evaporation and chemical composition
- Flash point
- Emulsification and emulsion stability
- Density
- Viscosity
- Dispersibility (natural or chemical dispersibility)
- Oil adhesion
- Treating agents (selection of dispersants and demulsifiers)
- Oil biodegradability

At the end of the weathering process, a dispersibility test could be performed directly in the canal as it seemed to provide more realistic results (Guyomarc'h *et al.*, 1999b).

Environmental conditions. All tests were run assuming a moderate situation (sea state 3, which corresponds to wave heights between 0.5 and 1.25 m). Air temperature was set at 10 and 20°C, but it was also possible to re-create the average annual temperature of the oil field if necessary (from 0 to 30°C). Solar energy was recreated by four UV lights (up to 40 W/m^2). Full salinity seawater (33 ppt) was used in tests.

Sampling procedure. The oil volume poured onto the water surface at the beginning of the test was set at 20 L to ensure an extensive sampling even in case of high evaporation rates and to account for oil that stuck on the tank walls. During the first 12 hours, one sample was collected at least every 2 hours; after that period, the intervals could be increased to 4 to 6 hours and, finally, remaining oil was sampled twice a day until the weathering time reached 1 week. (Table 1).

Measurements. All the methods used to assess or measure the various parameters have been previously presented (Guyomarc'h and Merlin, 2000).

Crude oils. Crude oils were supplied by TOTALFINA-ELF from different oil fields located around the world. Density and viscosity of these tested oils are shown in Table 2.

Flume test weathering: Examples of different evolutions

The various parameters were plotted versus the weathering time and, when possible, a curve was applied. This fit was the result of a statistical analysis using the Sigmaplot 4.0 software (SPSS Inc.). The data presented below come from different products and provide examples of different evolutions that were observed considering various parameters: influence of the oil nature, temperature, and UV lights.

Nature of the oil. The initial increase in viscosity was the result of either emulsification or evaporation, or both. For some oils, it was possible to point out that evaporation was mainly responsible for the increase in the first few hours: the water content was stable and low. Following this first phase, the oil was able to incorporate water up to 80%. On the other hand, some oils did not require a significant evaporation rate before incorporating water (Figure 2). Two different models (Figure 3) were applied according to the main phenomenon: an "exponential rise to the maximum" model for the emulsification and an "exponential growth" for the evaporation (Guyomarc'h and Merlin, 2000).

Considering the type of initial evolution, oils could be divided in two groups. Figure 4 illustrates the initial evaporation for three oils and shows that the duration of this phase depends on the nature of the product. In addition, the longer it is, the more viscous get the oil : this could be explained by the increase of the polar compounds content that allows a greater water uptake and stabilizes the emulsions. Figure 5 illustrates an immediate emulsification. Oils revealed also different kinetics and some rate constant were so low that in some cases it seemed that the increase was linear.

Temperature. The oils were weathered under the same conditions at two different temperatures. Surprisingly, after 48 hours in the flume, for most of cases, viscosity at 20°C was higher than at 10°C. Considering the type of evolution presented in Figure 6, it seemed that evaporation constituted a key factor. At 10°C, the oil incorporated some water at the beginning of the experiment and the following increase of viscosity was mainly due to evaporation. However, the emulsion was unfavorable to this process that was considerably slowed down. At 20°C, the oil initially evaporated and then, incorporated some water: the resulting emulsion was more viscous. The comparison of the water content evolution shown in Figure 7 seemed to be in agreement with this explanation: the rate constant of the kinetics was higher at 10°C than at 20°C but the maximum water content was 80% at 20°C compared to 75% at 10°C.

For one of the oils tested, the behavior at 10°C was very close to the one observed at 20°C (maximum water content: 55%, viscosity of 2,500 mPa.s after 1 week). In both cases, the evaporation process was very limited and the slight increase of polar content obtained at 20°C had a similar effect of making the temperature decrease down to 10°C.

UV lights. For two oils, the UV lights were switched on only after a weathering period of about two days. The same trend was observed, either at 10°C or 20°C (Figure 8): a second increase of viscosity was observed a few hours after this change of the environmental conditions. This was due to the photooxidation of some aromatic compounds into polar compounds (Barbas *et al.*, 1996) that stabilize the emulsion (Aomari-Badri, 1999). As a matter of fact, the volume of water that settled after the addition of a demulsifier decreased from 25% down to 0%.

Table 1. Sampling times.

Sample #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Time (hrs)	1	2	4	6	8	10	14	20	24	30	48	54	72	120	140

Table 2. Density and viscosity of the oils.

Oil origin	Density at 20°C	Viscosity at 10°C (mPa.s)	Viscosity at 20°C (mPa.s)
Angola	0.864	35	18
Saudi Arabia	0.855	35	9
United Emirates	0.847	13	7
Argentina	0.822	14	7
North Sea	0.864	28	20
Colombia	0.819	12	6

Open pools experiment

These tests were carried out in six floating mesocosms, each consisting of an area of 9 m² contained within a flexible boom fixed on a metallic structure, set in a sheltered harbor (Figure 9). The walls of the booms were flexible and the surface of the water was subjected to wind and agitation caused by the waves created by passing ships. The disposition of the device considering the prevailing wind is described in Figure 10.

Experimental procedure. The oil used in this experiment was an Arabian Light, partially evaporated (10%) due to safety reasons. It was characterized by a viscosity of 60 mPa.s at 15°C (mean temperature of the experiment).

At the beginning of the weathering, 20 liters were poured onto the water surface of the six mesocosms. Samples were collected after weathering periods of 1 and 3 days and brought back to the laboratory for viscosity, water content and evaporation determinations. The methods used were described previously (Guyomarc'h and Merlin, 2000); for the evaporation, among the different possibilities, the use of the Weathering Index (Fingas and Wang, 1994) seemed to be the most simple and reliable method.

Results. The evaporation rate was assessed by using the relationship obtained in the laboratory between the Weathering Index $W.I. = \frac{nC15+nC16+nC17+nC18}{nC25+nC26+nC27+nC28}$ and the evaporation rate ($\%_{Ev}$).

The equation was:

$$\%_{Ev} = -40.2 \times WI + 141.5$$

The results for the six mesocosms are presented Table 3 and the evolution of the average evaporation Figure 11. To assess the coherence of the evolutions, the viscosity was plotted versus the evaporation rate (Figure 12).

Discussion. The objective of this study was to obtain identical plots for treatment applications and also, to calibrate the flume test with "real data." The first objective needs a modification of the mesocosms' disposition as the most exposed to the wind were characterized by higher rates of evolution. These differences could be solved by disposing the mesocosms perpendicularly to the wind provided its direction is constant. The second aspect, in spite of a high dispersion of the results, revealed higher constant rates compared to the flume (evaporation, emulsification and water incorporation) but the maximum values were very similar. Concerning the evaporation process, the same oil weathered in the flume had lost its volatile compounds within the first 12 hours. The constant rate was between 4 and 6 times higher in the pilot scale experiment. The evolution of the water content followed the same trend and the same kind of ratio was found. However, the maximum viscosity was 5,500 mPa.s for the test in the hydraulic canal after 7 days compared to the mean value of 7,400 mPa.s after 3 days for the open pools. This could be due to the photooxidation process that cannot be entirely and realistically simulated in the canal.

Conclusion

The methodology for oil weathering studies applied in the flume provides several elements on oil behavior and evolution in specific environmental conditions in order to simulate more realistically the oil weathering process. They will be used by oil companies and responders to implement the response plan in case of oil spills.

The evolutions of the oils tested in the flume canal, considering only six products, revealed very different kinds of behavior. This was mainly due to the balance between the evaporation and emulsification processes. The predominance of one on the other varied with the nature of the oil and also, for the same products, with the temperature. In all the cases, viscosity at 20°C was higher than at 10°C. Finally, the photooxidation proved to increase viscosity in an important way.

The flume calibration in real conditions at sea in floating mesocosms, despite a dispersion of the data, made it possible, for one oil, to assess the difference of kinetics, particularly concerning the emulsification and evaporation processes. This demonstrated that the hydraulic canal sped up the phenomenon (ratio between 4 and 6). This experiment at sea pointed out also the influence of the photooxidation that is of great importance and which should not be underestimated in experimental simulations.

Acknowledgements

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Table 3. Viscosity, water content, and evaporation at day 1 and day 3 (floating mesocosms experiment).

Mesocosm #	1	2	3	4	5	6
Viscosity (mPa.s)	1,880	280	410	370	2150	280
	10,200	7,200	9,400	6,200	6,100	5,200
Water Content (%)	66	32	34	40	50	29
	73	72	71	61	61	59
Evaporation (%)	20.7	17.5	13.5	14.3	22.7	17.1
	>30	25.1	27.6	17.9	24.7	18.3

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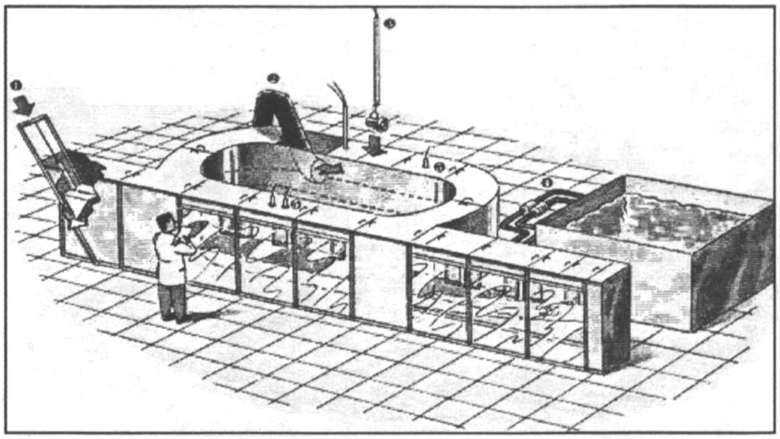

Figure 1. The hydraulic canal: the Polludrome.

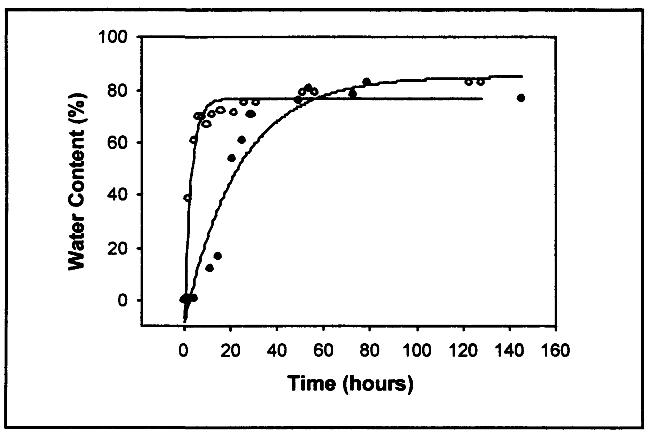

Figure 2. Evolutions of water content at 20°C for two different oils.

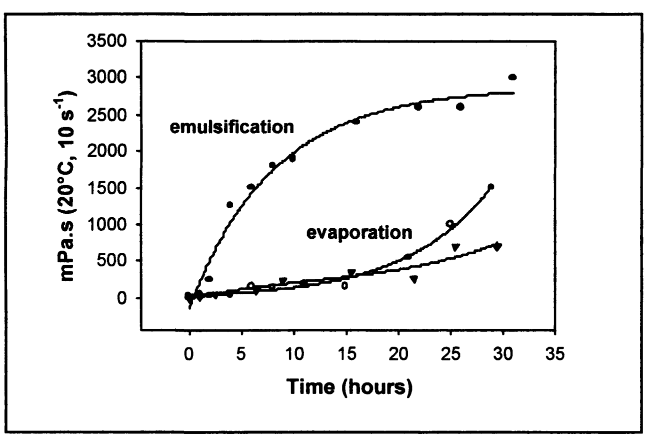

Figure 3. Initial increase of viscosity at 20°C: Influence of evaporation or emulsification.

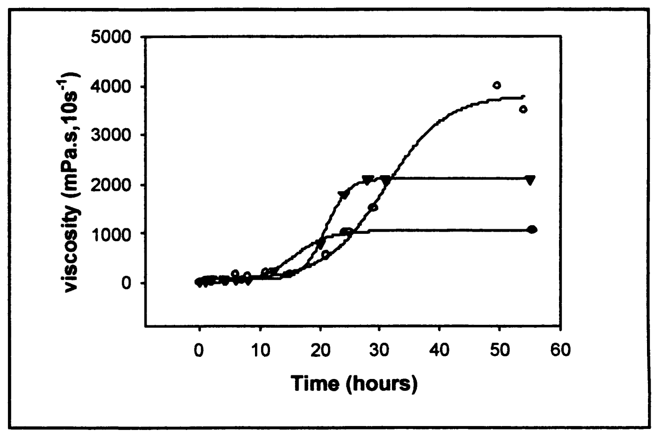

Figure 4. Prevalence of evaporation in the initial phase: Variations according to the oil nature (20°C).

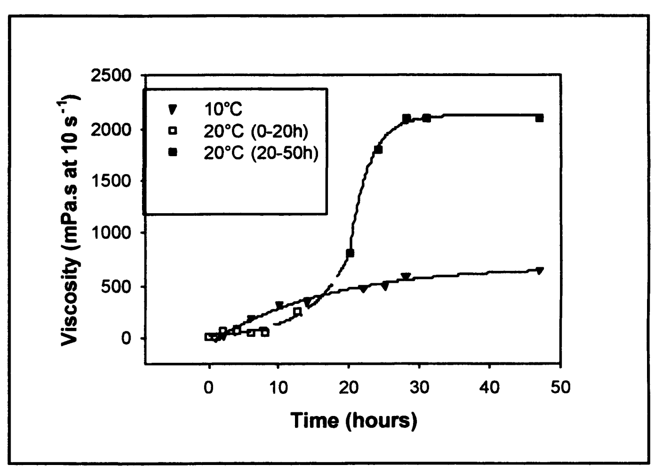

Figure 5. Prevalence of emulsification in the initial phase: Variations according to the oil nature (20°C).

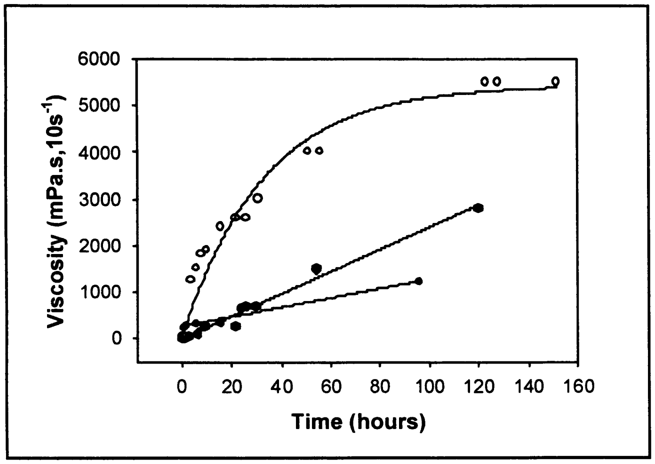

Figure 6. Evolution of viscosity for the same oil at 10 and 20°C.

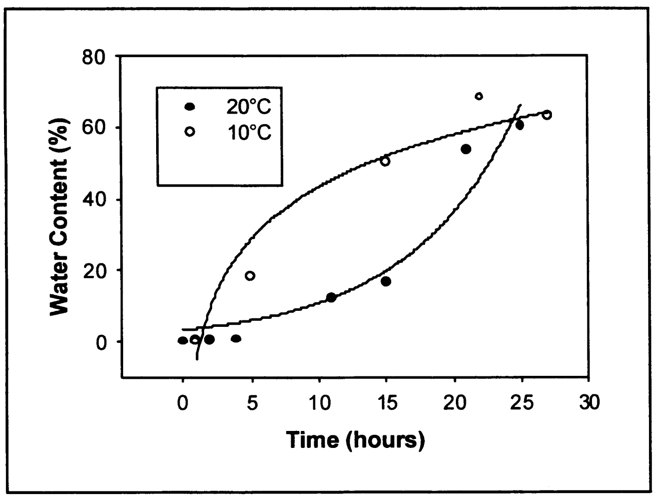

Figure 7. Evolution of water content for the same oil at 10 and 20°C.

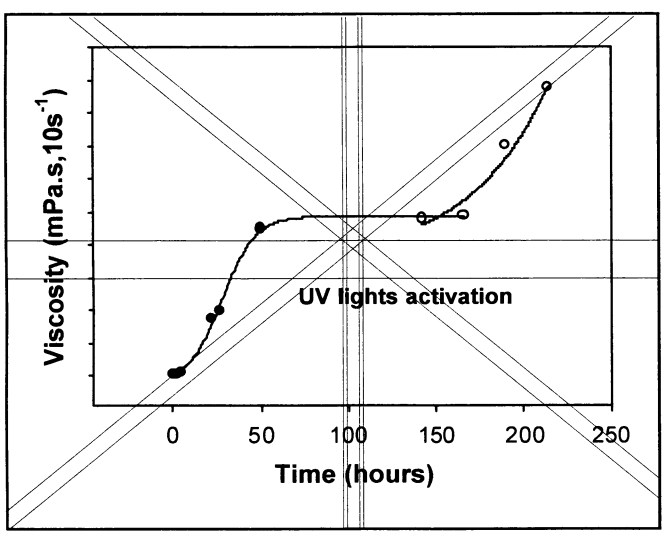

Figure 8. Influence of photooxidation (20°C).

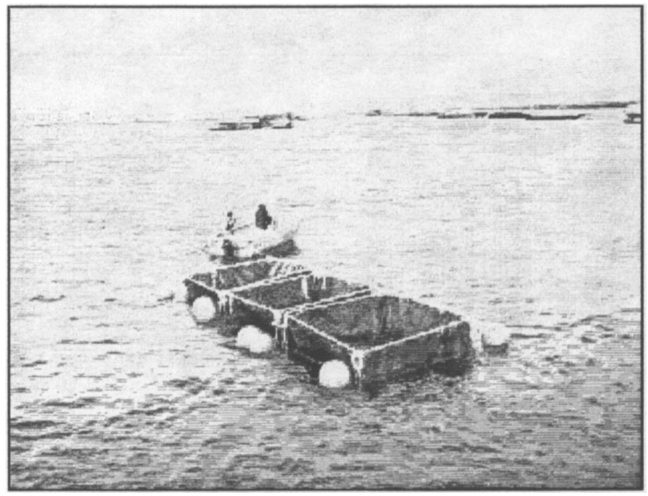

Figure 9. Floating mesocosms being towed to the experimental site.

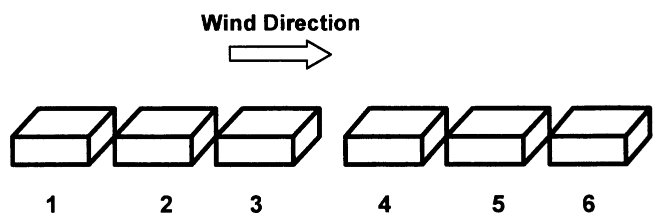

Figure 10. Disposition of the mesocosms.

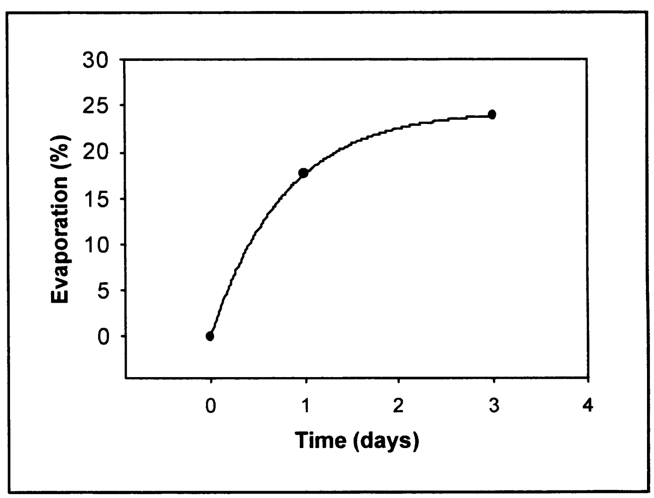

Figure 11. Evolution of evaporation versus weathering time.

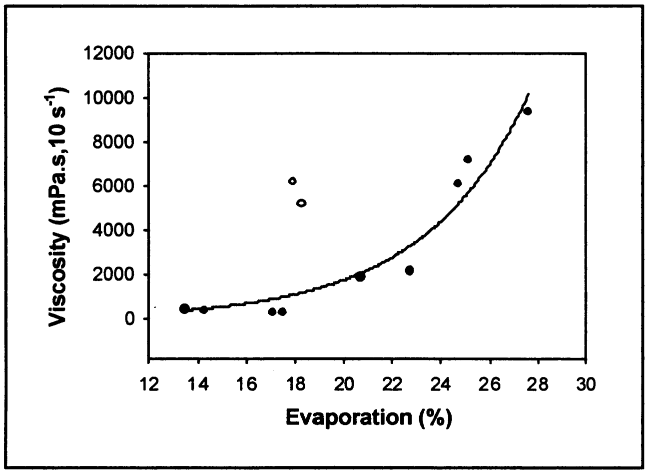

Figure 12. Evolution of viscosity versus evaporation.