BNL--48560

DE93 009878

QUARTERLY REPORT

BPO EOR FY 1993 (10/01/92 - 12/31/92)

TITLE: Effects of Selected Thermophilic Microorganisms on Crude Oils at Elevated Temperatures and Pressures

CONTRACT NO.: AS-219-ECD

CONTRACTOR: Associated Universities, Inc., Brookhaven National Laboratory

PRINCIPAL INVESTIGATORS: E. T. Premuzic and M. S. Lin

OBJECTIVES OF RESEARCH PROJECT

The objective of this program is to determine the chemical and physical effects of thermophilic and thermoadapted organisms on crude oils and cores at elevated temperatures and pressures. Ultimately a data base will be generated which will be used in technical and economic feasibility studies leading to field applications.

SUMMARY OF PROGRESS

1. Construction of Core-flooding Systems

We have reported (Premuzic and Lin, 1992) on the construction of a first-generation core-flooding system. The core bioreactor which was constructed from a 304 stainless steel 1-1/4" x 12" tube with a thickness of 0.065 inches, and can be operated safely up to a pressure of 2600 psi, is diagrammatically shown in Figure 1. Berea sandstone (200 Milli-darcys) has been cut and fitted into the stainless steel tube "bioreactors" . A sample of Wilmington, CA, crude oil (Table 1) was used in several experiments in which BNL organisms known to bioconvert this crude oil have been tried out in the core-flooding experiments.

Table 1. Data from Routine Analyses of Wilmington, CA, Crude Oil (Bartlesville Sample 71052)*

gravity, °API, 19.4
gravity specific, 0.938
sulfur percent 1.59

*(Dooley et al., 1974.)

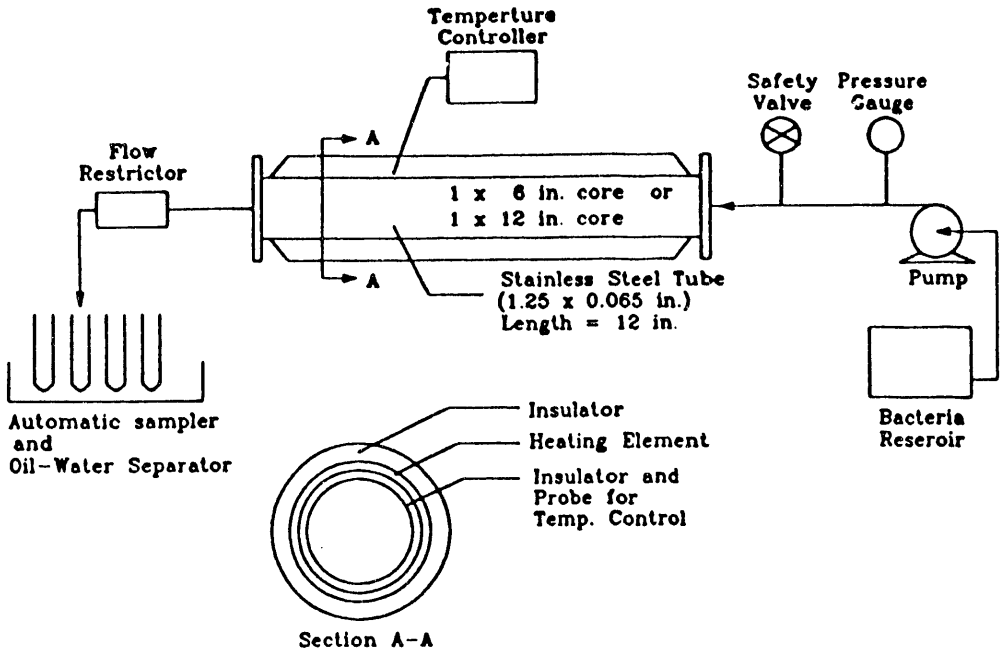

Figure 1 - Flow Diagram for Core-flooding Bioreactor.

The results of the first series of core-flooding experiments with five microorganisms from the BNL collection are given in Table 2 in this series of experiments.

Table 2
Recovery of Wilmington Crude from Brea Sandstone Cores at 65°C.

	1	2	3	4	5
Core absorbed oil sample, wt. (g)	16.3	16.3	16.7	16.7	16.7
Pressure (psi)	44	44	44	30	30
Microorganisms	BNL-NZ-3	-4-23	-4-22	TAQ-2	TAQ-1
Surface tension of culture (dynes/cm)	70.7	70.0	70.0	70.7	62.7
Oil recovered by brine (g)	5.2	7.6	8.9	5.7	7.8
Oil recovered by growing microorganisms (g)	5.7	3.7	2.8	3.2	4.1
Oil recovery by brine (%)*	31	47	53	34	47
Additional oil recovery by growing microorganisms (%)**	50	43	36	29	46

$$* \quad \% \text{ Oil recovery by Brine} = \frac{\text{oil recovered by brine (g)}}{\text{oil sample wt. (g)}} \times 100$$

** % Additional oil recovered by growing microorganisms =

$$\frac{\text{oil recovered by microorganisms (g)}}{\text{oil sample wt. (g)} - \text{oil recovered by brine (g)}} \times 100$$

The results from the first of core-flooding experiments show a significant additional oil recovery under the experimental conditions used. In this series of tests different conditions and different heavy crude microorganisms systems will be examined.

2. Duration of Biotreatment and Media Effects

Studies of trends in biochemical interactions between different microorganisms and crude oils continue.

Studies with two different crude oils which have not been previously investigated have been initiated. These include an Arkansas crude (°API=20, S=4.2%) and Alabama crude (°API=19, S=4.6%). The results of tests with the Arkansas crude are given in Tables 3 and 4 and in Figures 2 and 3. In the presence of tergitol, BNL-4-23 appears to be an efficient bioconverter over a period of seven days. The controls are oil + medium + detergent (oil-C), oil + medium (control-C), and organisms + medium + tergitol (BNL-#-C). In the absence of tergitol, BNL-4-23 appears to be a weaker emulsifier and requires a longer period of time to be effective. However, Gas Chromatography-Mass Spectrometry (GC-MS) analyses and the corresponding gas chromatography analyses equipped with a Flame Photoemission Detector (FPD) indicate little or no change due to the biotreatment as shown in Figures 4 and 5, although relative to the control there is some decrease in the overall content of organosulfur components of the crude. These results may be interpreted in the following manner. The biotreatment of Arkansas crude with BNL-4-22 and BNL-4-23 does produce emulsification and some changes in the sulfur content, which could be due to small chemical changes causing an overall redistribution and alteration in mutual solubility of major fractions. To explore further the feasibility of such processes occurring, a sample of Arkansas crude was treated with BNL-NZ-3, an efficient bioconvertor of Monterey crude, particularly A851 (see Premuzic et al., 1993, 1992). The results are presented in Table 5 and Figures 6 and 7. Thus, small changes do appear in the scan region of 1200 to 3000, particularly evident in the expanded scan of the 2100 to 3600 region, and even more evident in the FPD chromatograms shown in Figure 8. Analogous experiments and testing with Alabama crude are currently underway.

3. Microscopic Comparison of Reaction Mixtures (RMs)

Results obtained from comparative studies of interaction between different crude oils and microorganisms deliberately introduced for the purpose of biotreatment continue to suggest that the biochemical process(es) may be predominately driven by the introduced and not indigenous microorganism (see present report). Microscopic comparison is continuing and observable microscopic changes are shown in Figures 9 through 12 for Monterey oils in the presence and the absence of tergitol. The differences between "indigenous" effects and "introduced" effects are evident.

Table 3. Biotreatment of Arkansas B70116 Crude in Medium 3* in the Presence of a Detergent (Tergitol) Over a Period of Seven and Twenty Days.

Microorganisms	Detergent	Medium	%Oil	Incubation (Days)	Kletts Units (OD x 500)	pH
BNL-4-22	YES	Medium 3	0.497	7	17.300	4.00
BNL-4-22-C	YES	Medium 3	0.000	7	51.800	4.25
BNL-4-23	YES	Medium 3	0.513	7	142.000	4.00
BNL-4-23-C	YES	Medium 3	0.000	7	61.950	4.00
Oil-C	YES	Medium 3	0.494	7	27.850	4.00
Control-C	YES	Medium 3	0.000	7	10.500	4.25
BNL-4-22	YES	Medium 3	0.516	20	43.000	3.50
BNL-4-22 Control	YES	Medium 3	0.000	20	26.000	3.50
BNL-4-23	YES	Medium 3	0.518	20	61.500	3.50
BNL-4-23 Control	YES	Medium 3	0.000	20	15.000	3.50
Control, Oil	YES	Medium 3	0.510	20	15.500	3.50
Control/Control	YES	Medium 3	0.000	20	19.500	3.50

*Premuzic and Lin, BNL #48381, 1992.

Table 4. Biotreatment of Arkansas B70116 Crude in Medium 3 in the Absence of a Detergent Over a Period of Seven and Twenty Days.

Microorganisms	Detergent	Medium	%Oil	Incubation (Days)	Kletts Units (OD x 500)	pH
BNL-4-22	NO	Medium 3	0.519	7	5.000	3.50
BNL-4-23	NO	Medium 3	0.588	7	0.500	3.50
Control, Oil	NO	Medium 3	0.500	7	0.000	3.50
BNL-4-22 Control	NO	Medium 3	0.000	7	5.000	3.50
BNL-4-23 Control	NO	Medium 3	0.000	7	0.500	3.50
Control/Control	NO	Medium 3	0.000	7	0.000	3.50
NO DETERGENT EXP III						
BNL-4-22 Control	NO	Medium 3	0.489	20	38.750	4.25
BNL-4-23 Control	NO	Medium 3	0.479	20	54.595	4.25
Control, Oil	NO	Medium 3	0.526	20	13.625	4.25
BNL-4-22 Control	NO	Medium 3	0.000	20	14.595	4.25
BNL-4-23 Control	NO	Medium 3	0.000	20	5.365	4.00
Control/Control	NO	Medium 3	0.000	20	9.710	4.00

Table 5. Arkansas B70116 Crude Biotreated with BNL-NZ-3.

Microorganisms	Detergent	Medium	%Oil	Incubation (Days)	Kletts Units (OD x 500)	pH
BNL-NZ-3	NO	Medium 3	0.532	7	3.16	4.5

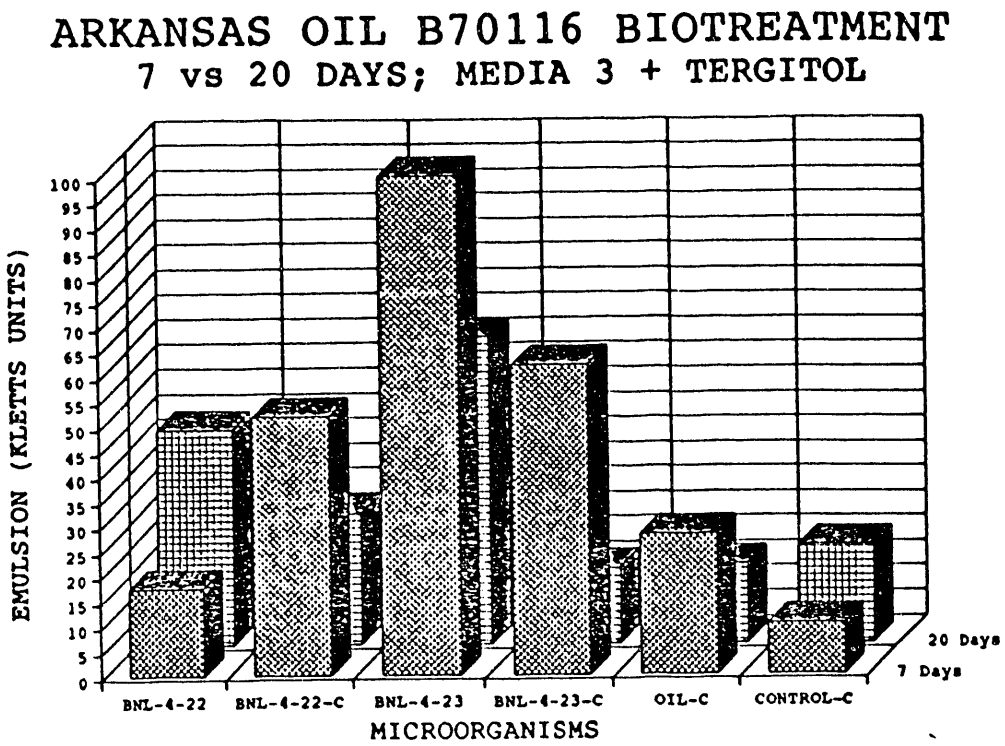

Figure 2

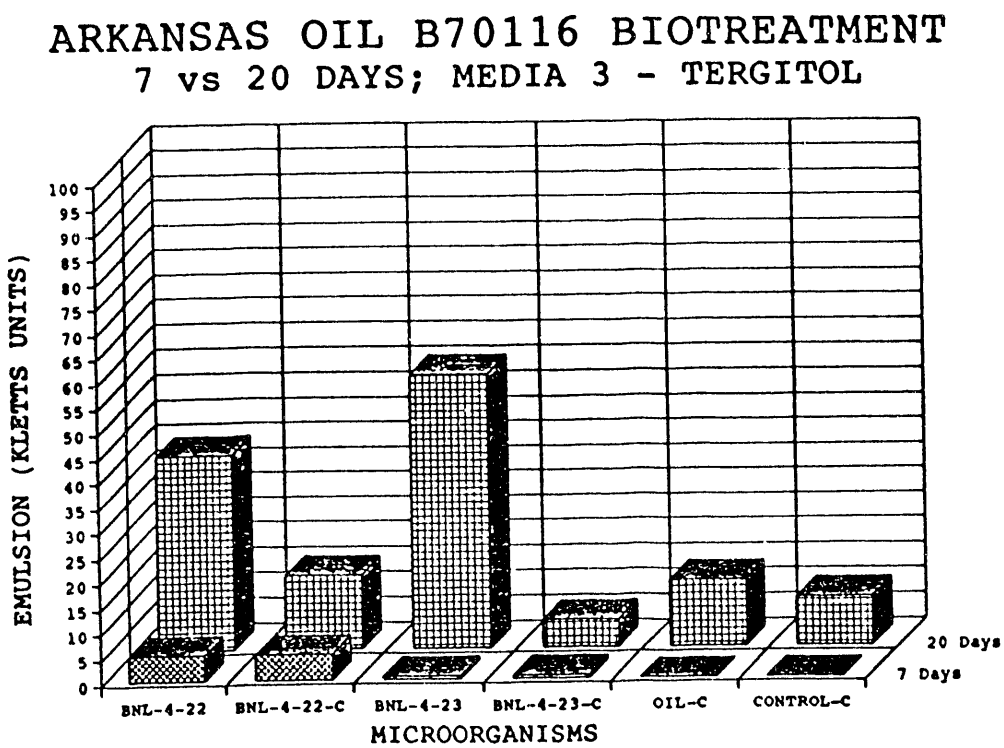

Figure 3

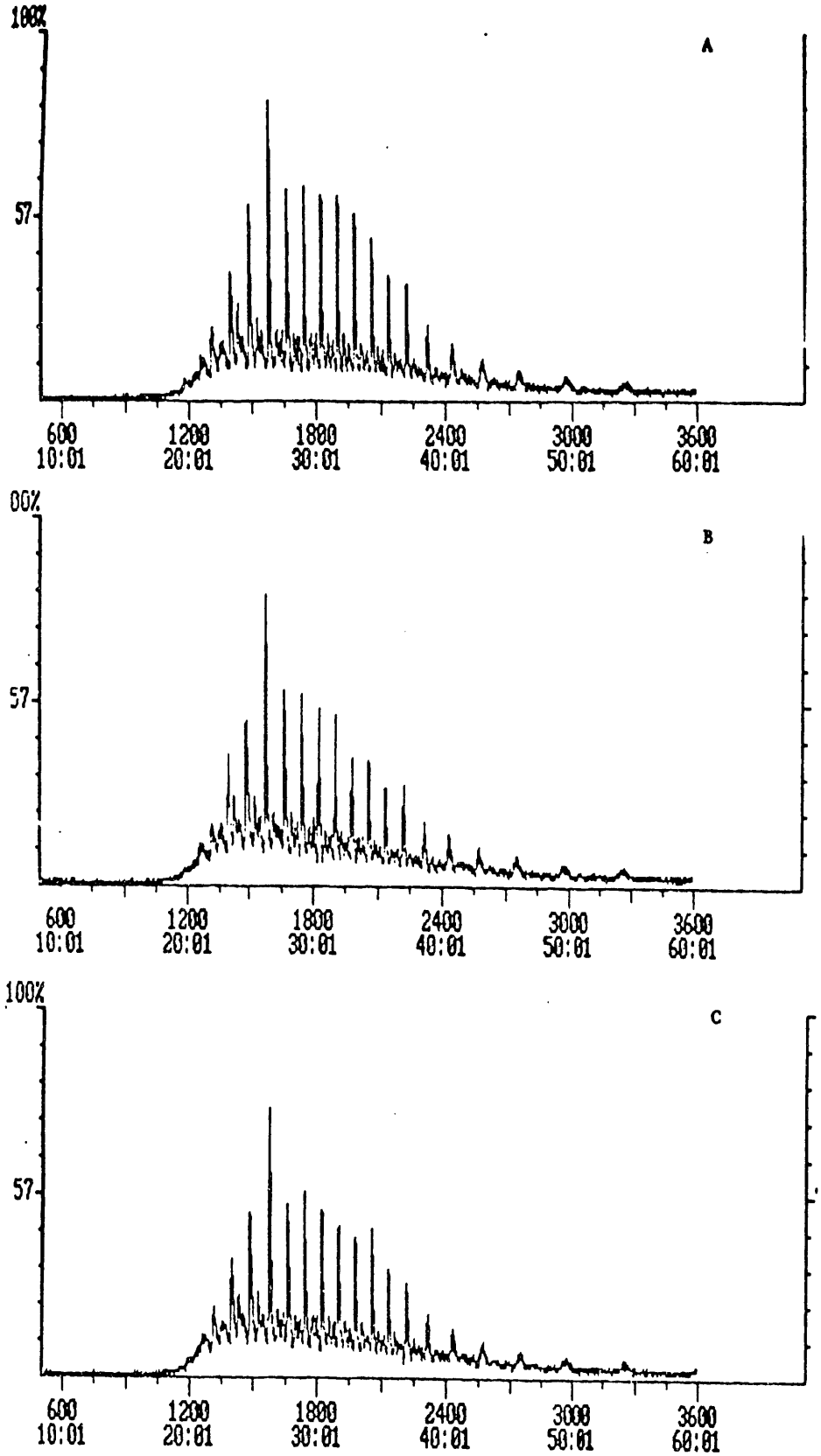

Figure 4. Arkansas B70116, A: Control; B: Treated with BNL-4-22; C: Treated with BNL-4-23.

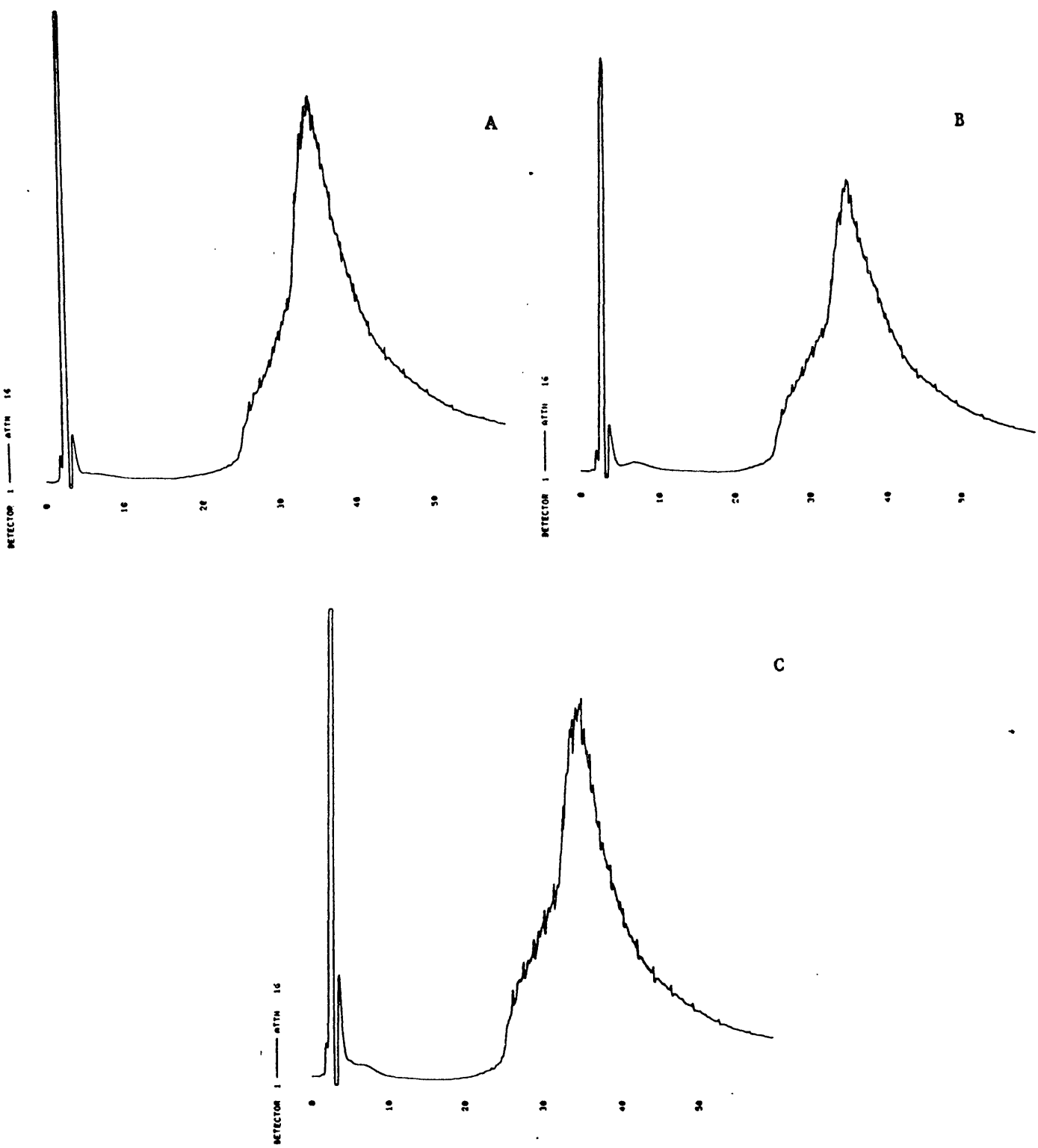

Figure 5. Chromatograms, Flame Photoemission Detector (FPD) trace of Arkansas B70116, A: Control; B: Treated with BNL-4-22; C: Treated with BNL-4-23.

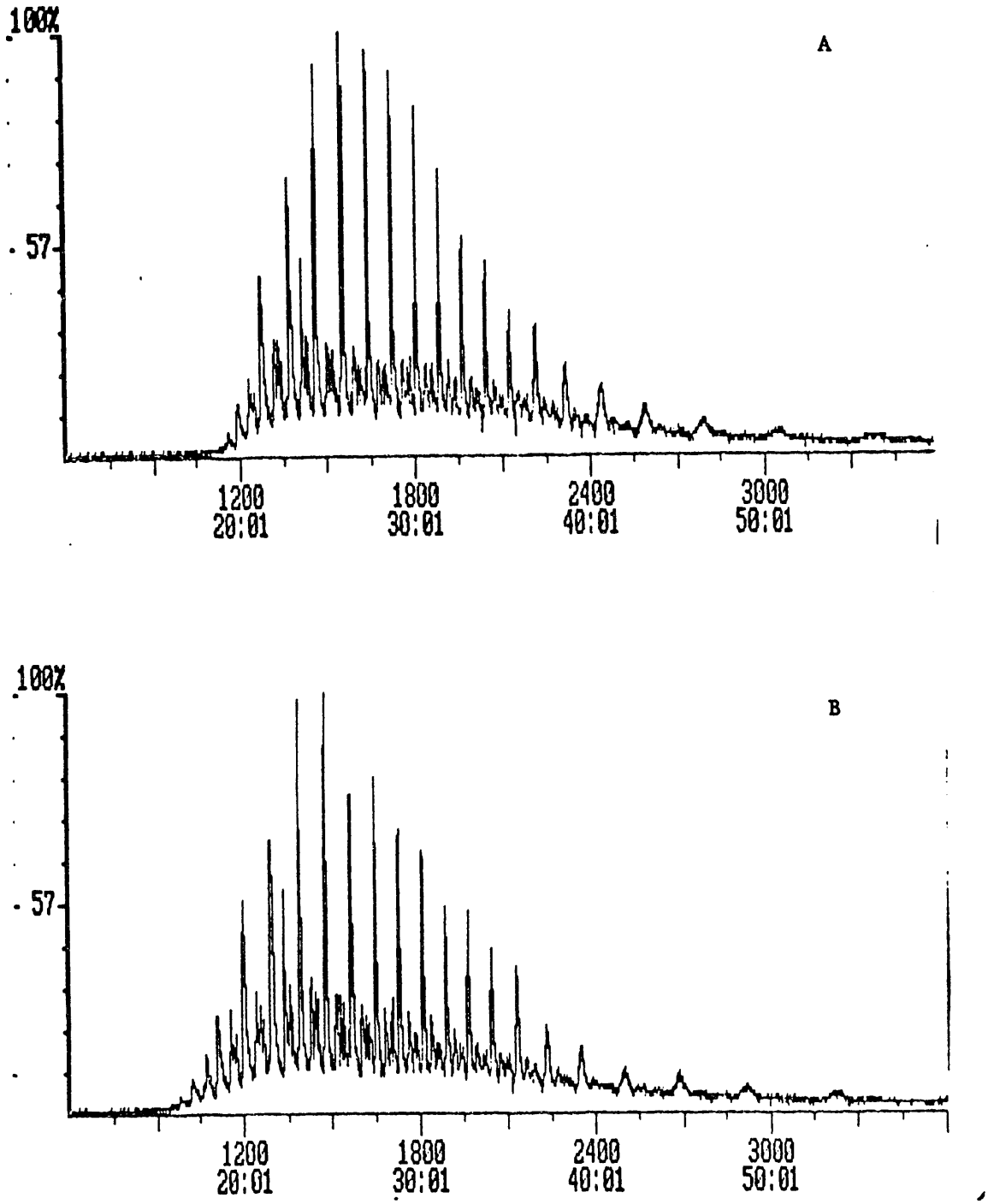

Figure 6. Arkansas B70116 Gas Chromatographic-Mass Spectrometry (GC-MS) fragmentograms, A: Control; B: Treated with BNL-NZ-3.

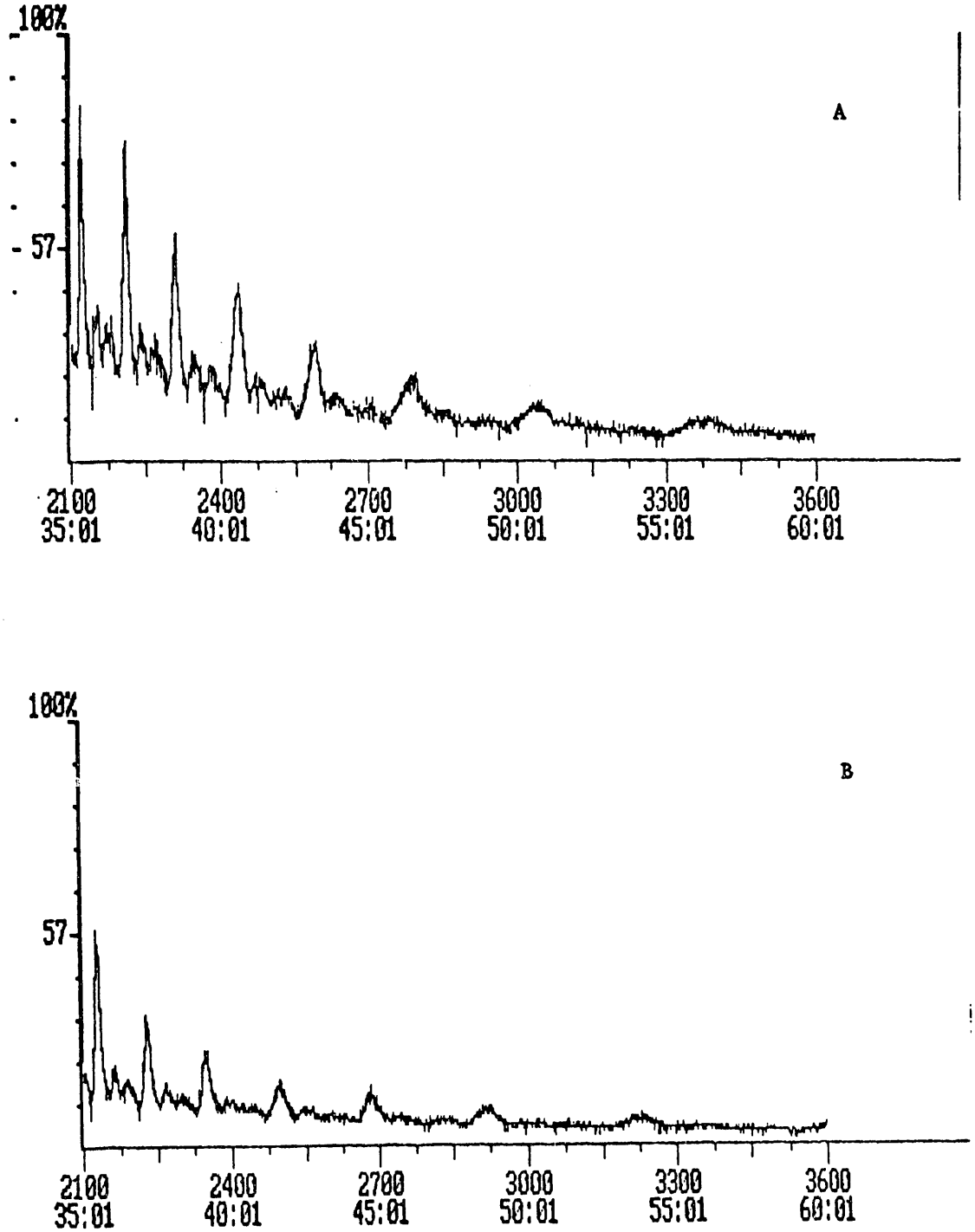

Figure 7. Arkansas B70116 Gas Chromatographic-Mass Spectrometry (GC-MS) fragmentograms expanded scans (2100-3600). A: Control; B: Treated with BNL-NZ-3.

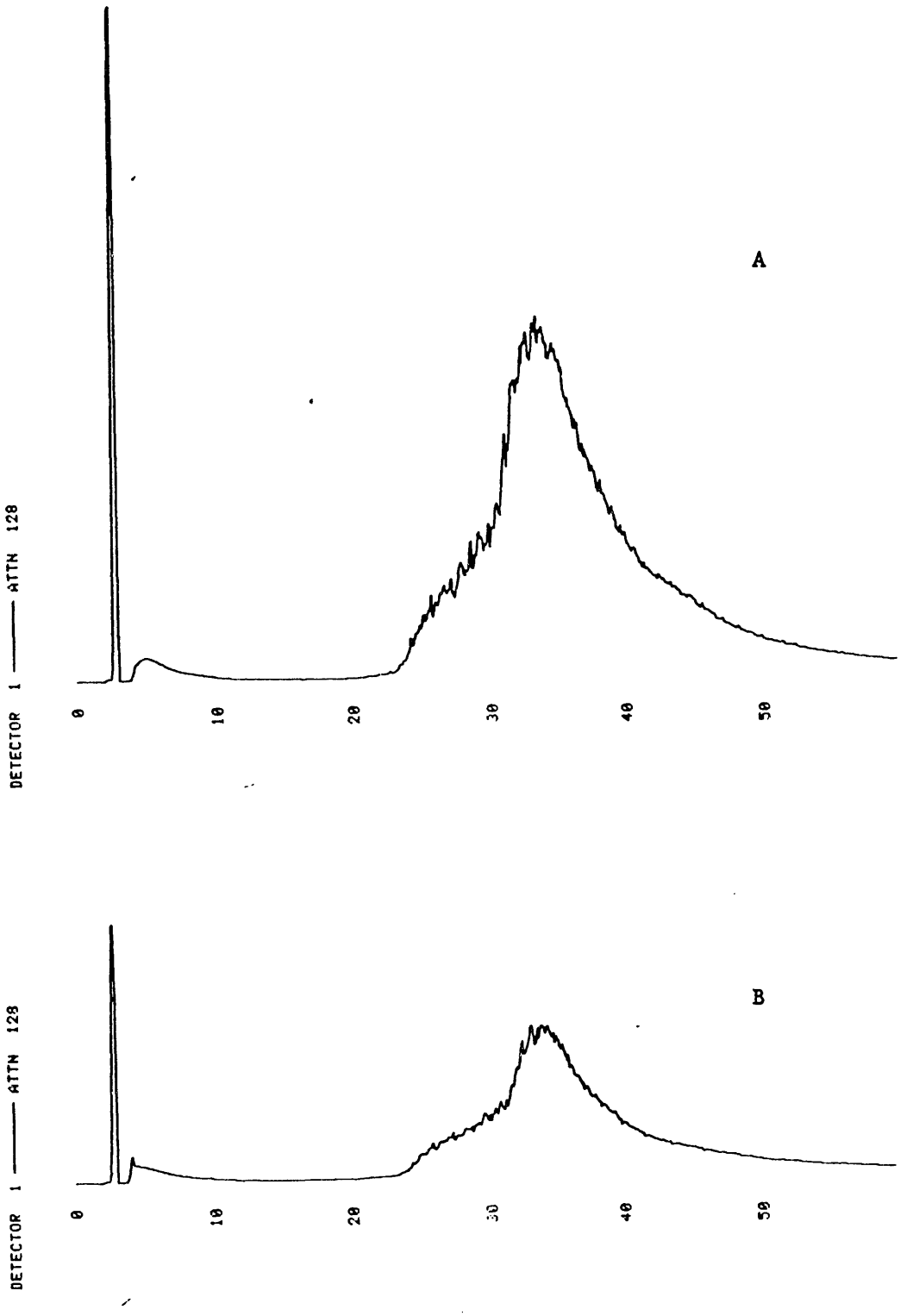

Figure 8. Chromatograms, Flame Photoemission Detector (FPD) trace of Arkansas B70116, A: Control; B: Treated with BNL-NZ-3; seven days, medium 3, no tergitol.

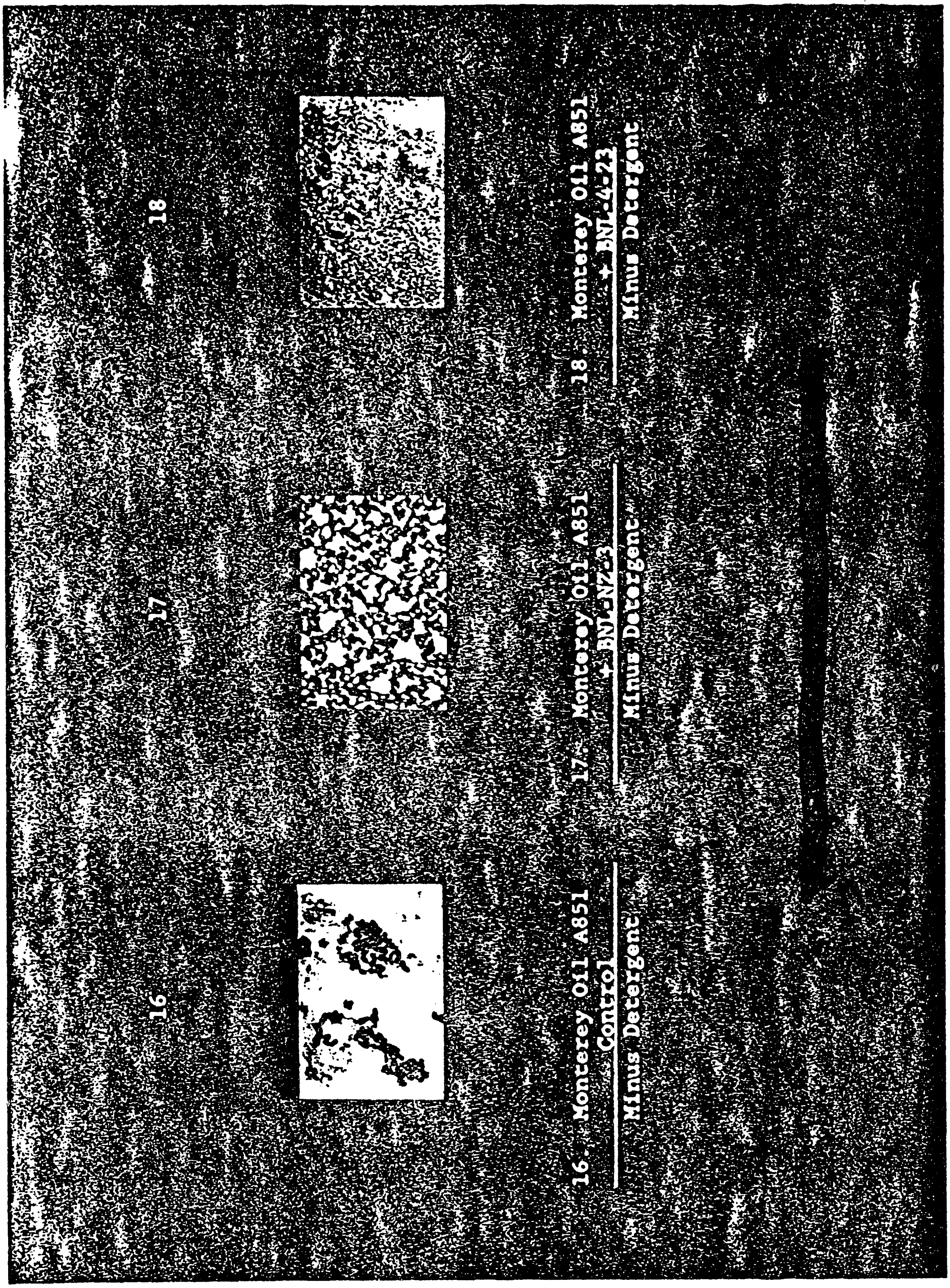
16
17
18
16. Monterey Oil A851
Control
Minus Detergent
17. Monterey Oil A851
+ BNL-NZ-3
Minus Detergent
18. Monterey Oil A851
+ BNL-4-23
Minus Detergent

Figure 9

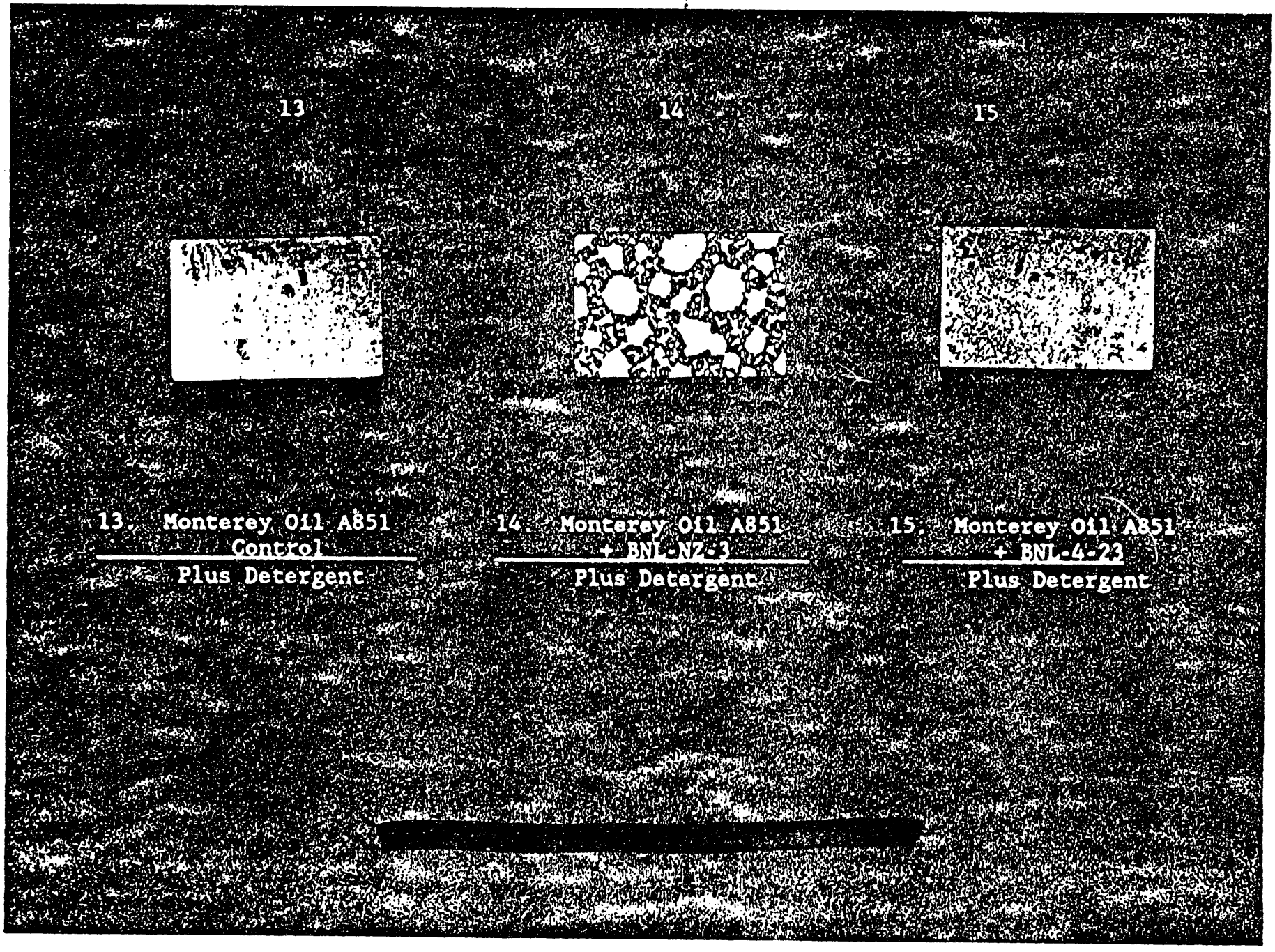
13
14
15
13. Monterey Oil A851
Control
Plus Detergent
14. Monterey Oil A851
+ BNL-NZ-3
Plus Detergent
15. Monterey Oil A851
+ BNL-4-23
Plus Detergent

Figure 10

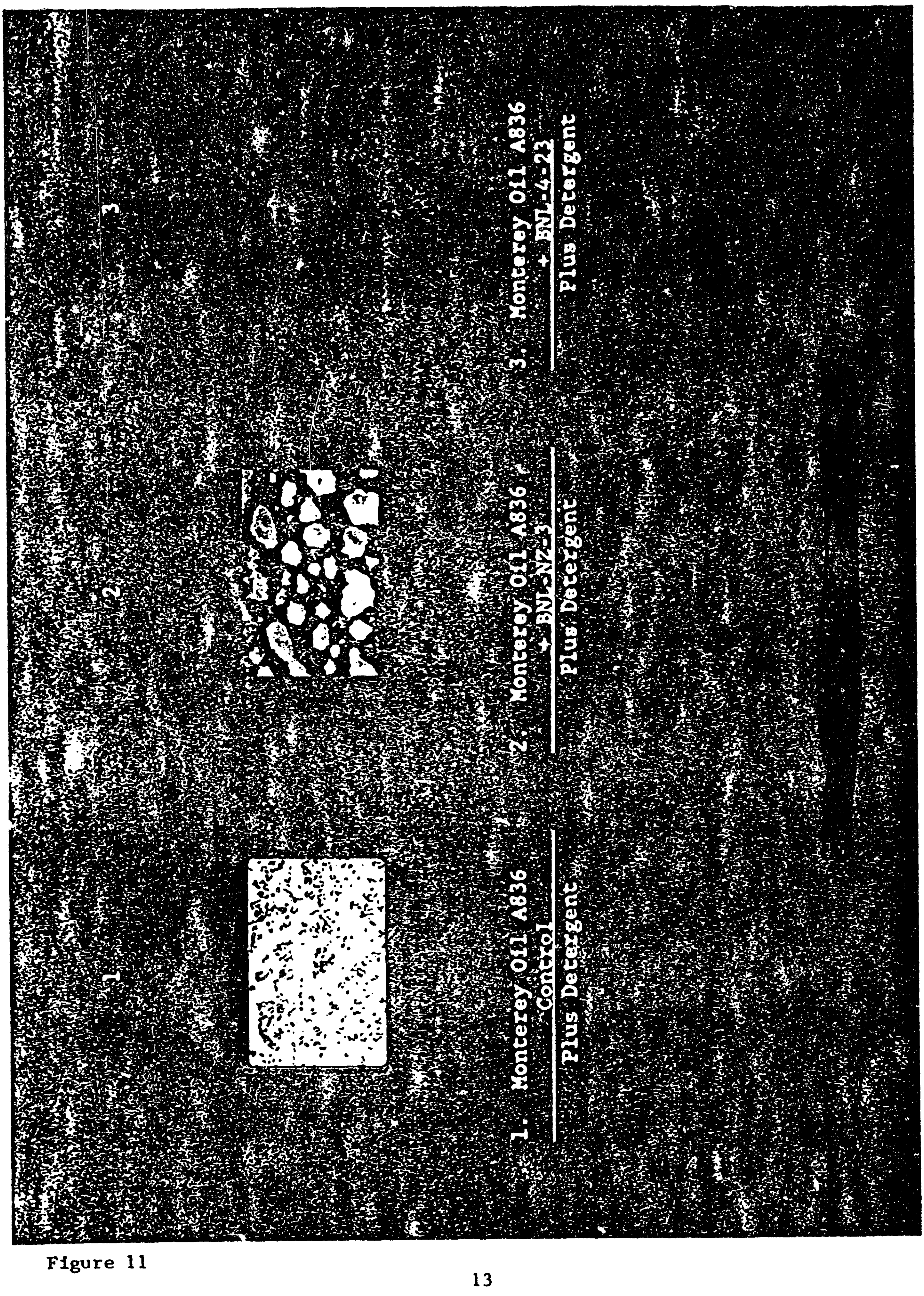
1
2
3
1. Monterey Oil A836
Control
Plus Detergent
2. Monterey Oil A836
+ BNL-N2-3
Plus Detergent
3. Monterey Oil A836
+ BNL-4-23
Plus Detergent

Figure 11

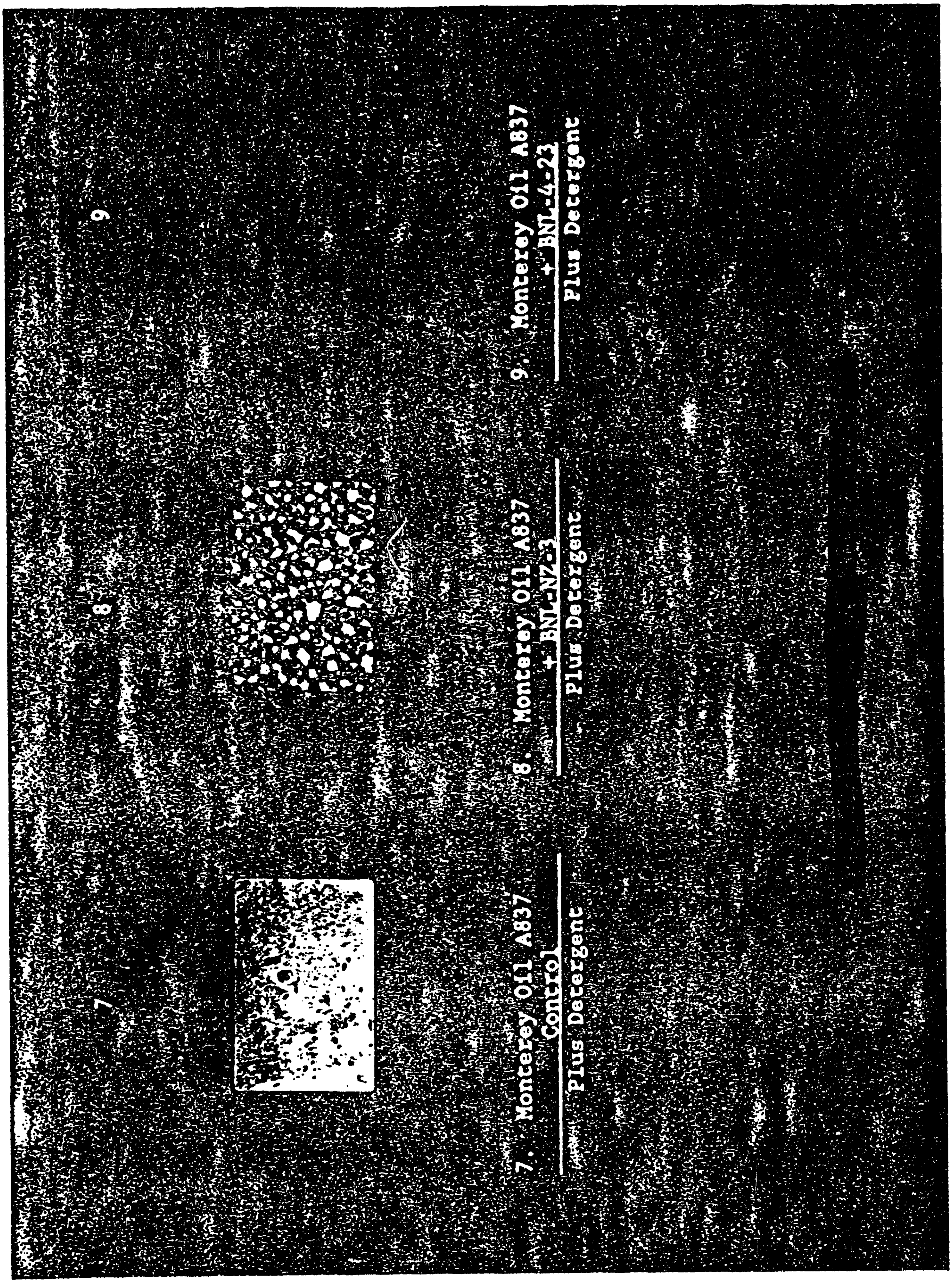
7. Monterey Oil A837
Control
Plus Detergent
8. Monterey Oil A837
+ BNL-NZ-3
Plus Detergent
9. Monterey Oil A837
+ BNL-4-23
Plus Detergent
7
8
9

Figure 12

4. Invited Presentations

Premuzic, E. T., Lin, M. S., and Manowitz, B. Comparison of biochemical microbial effects in enhanced oil recovery (MEOR) (extended abstract). To be presented at the American Chemical Society Spring 1993 Conference, Denver, March 28-April 2, 1993.

Premuzic, E. T., Lin, M. S., and Manowitz B. Parallel trends in the biotreatment of fossil fuels (abstract). To be presented at the American Chemical Society Conference, Denver, March 28-April 2, 1993.

Premuzic, E. T., Lin, M. S., and Manowitz, B. Diagnostic significance of chemical markers in bioprocessing of crude oils (abstract). To be presented at the American Chemical Society Conference, Denver, March 28-April 2, 1993.

Premuzic, E. T., Lin, M. S., and Manowitz, B. Biochemical alteration of crude oils in microbial enhanced oil recovery (abstract). To be presented at the International Biohydrometallurgy Symposium, Jackson Hole, WY, Aug. 1993.

REFERENCES

Premuzic, E. T., and Lin, M.S. Effects of selected thermophilic microorganisms on crude oils at elevated temperatures and pressures. Quarterly Report (07/01/92-09/30/92) BNL 48381, Sep 1992.

Dooley, K. E. Hirsch, D. E., Thompson, C. J., Vogh, J. W., and Ward. C. C. Distillate of Wilmington, CA, crude oil. Hydr. Proc., 53(7) p. 141, 1974.

Premuzic, E. T. and Woodhead. A., ed., Fourth International Conference on Microbial Enhanced Oil Recovery, Elsevier Publ. Co., Amsterdam, 1993. in preparation.

END

DATE
FILMED
4/30/93