

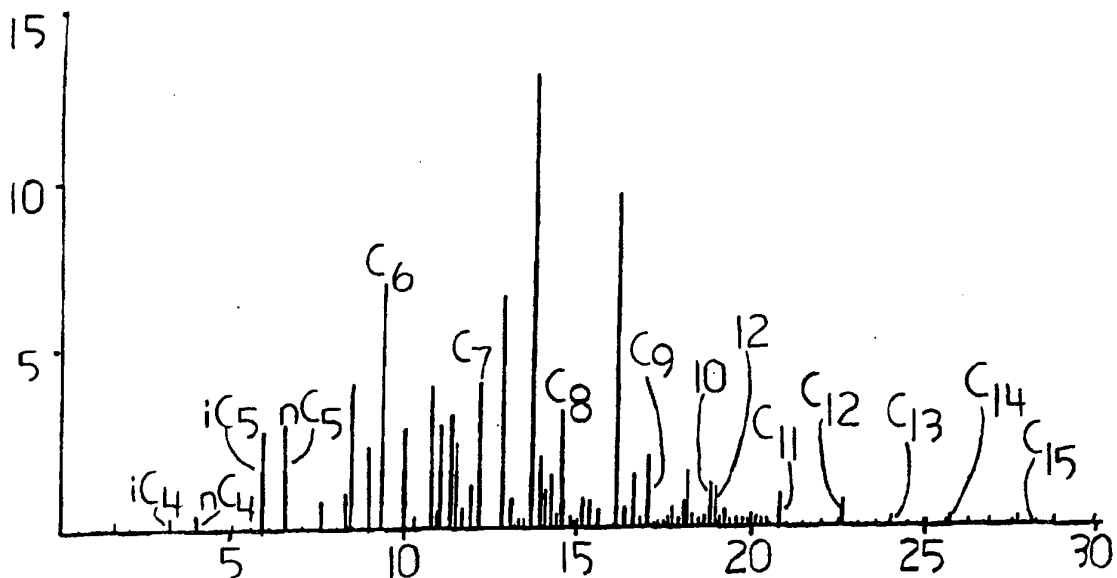


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : E21B 37/06</p>	<p>A2</p>	<p>(11) International Publication Number: WO 94/19575 (43) International Publication Date: 1 September 1994 (01.09.94)</p>
<p>(21) International Application Number: PCT/CA94/00109 (22) International Filing Date: 24 February 1994 (24.02.94) (30) Priority Data: 2,090,306 24 February 1993 (24.02.93) CA (71) Applicant: TRY SOL LIMITED [CA/CA]; 630 - 6th Avenue S.W., 12th floor, Calgary, Alberta T2P 0S8 (CA). (72) Inventors: THORSSSEN, Donald, A.; 12016 Lake Erie Way S.E., Calgary, Alberta T2J 2M1 (CA). LOREE, Dwight, N.; 758 Woodpark Road S.W., Calgary, Alberta T2X 2S4 (CA). (74) Agent: LAMBERT, Anthony, R.; Thompson Lambert, #204, 10328 - 81 Avenue, Edmonton, Alberta T6E 1X2 (CA).</p>		<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i></p>

(54) Title: OIL WELL WAX REMOVAL FLUID

AMPLIFICATION



COMPOSITION

(57) Abstract

A wax and asphaltene solvation fluid for use in oil and gas wells is derived as a residual fluid from a feedstock that includes a greater mass percentage of trimethylbenzene than decane, and is preferably sour. Mass percentage of both aromatics and asphaltenes in the residual fluid is in the 30 % - 70 % range, and a complex mixture of both is described.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

TITLE: OIL WELL WAX REMOVAL FLUID

INVENTORS: DONALD A. THORSSSEN AND DWIGHT N. LOREE

5

FIELD OF THE INVENTION

This invention relates to oil and gas well operation fluids, particularly those used for the removal of contaminants from wells.

10

BACKGROUND AND SUMMARY OF THE INVENTION

The rocks that contain oil and gas in oil and gas reservoirs are porous and to remove the oil or gas from the reservoirs requires that the oil or gas move through the pores in the rock. If the pores are blocked, then it is difficult and it may even become impossible to remove the oil or gas from the reservoir, with consequent economic loss to the oil or gas well owner.

15

20

Two notorious contaminants that may block the pores are waxes and asphaltenes. A wax is normally defined as a hydrocarbon that is a solid at room temperature and has 20 carbon atoms or more. An asphaltene is an agglomerate of aromatic hydrocarbons, and may contain bound oxygen, nitrogen and sulphur atoms. The oil and gas in many, if not most, reservoirs contains both waxes and asphaltenes. These waxes and asphaltenes may be dissolved in the oil. In some cases, however, the waxes and asphaltenes may partially block the pores, or, as production continues, the very action of removing oil from a reservoir may cause waxes and asphaltenes to precipitate out of solution and block the pores.

25

30

35

Also, the waxes and asphaltenes may precipitate out of solution in the well bore itself,

or in equipment used for the production of oil and gas and reduce or block the flow of oil from the well.

5 The economic damage from waxes and asphaltene precipitation can be very high, killing some wells entirely. Consequently, a great deal of attention has been devoted to developing cost effective ways of preventing waxes and asphaltenes from precipitating out of solution or of removing the waxes and asphaltenes from an oil reservoir or well
10 bore.

One such attempt at a solution has been to apply to a well a mixture of a significant proportion of the aromatic xylene (about 45%) and a lesser proportion of the paraffinic hydrocarbon hexane (about
15 30%), together with about 25% methanol. This product is known by the name NP760 and is available from Wellchem of Calgary, Alberta, Canada. The xylene is intended to solvate asphaltenes and the hexane is intended to solvate waxes. The xylene and hexane
20 components of the composition are each derived from refining a feedstock and removing that particular component from the feedstock. The result is a product that has moderate success in solvating at least some waxes and asphaltenes, but because the fluid is made
25 from a complex process, the fluid is relatively expensive.

One difficulty with the use of hexane or other alkanes is that they tend to cause asphaltenes to precipitate out of solution. This in turn is
30 believed to increase the precipitation of waxes. How this is believed to occur is as follows. Waxes require nucleation sites in the oil formation or well bore to which they can attach. Any such site will become a nucleation site for the further accretion of waxes. In

time, the waxes, mixed with asphaltenes, build outward and block the well bore or pores in the formation. In a typical oil formation water surrounds the rock in the formation and waxes will tend to slide off the water and not attach to the rock. However, if asphaltenes are present, they may attach to the rock surface since reservoir rock contains positively and negatively charged molecules (cations and anions) which attract the polar asphaltenes. The asphaltenes may then protrude beyond the water layer surrounding the rock particle and form a nucleation site for waxes. Hence a precondition for wax deposition is the precipitation of asphaltenes from the oil in the reservoir. It is the hexane that causes the precipitation of the asphaltenes and thus the formation of nucleation sites for waxes. The xylene is added to solvate the asphaltenes and prevent the formation of nucleation sites.

However, such a product, formed of an alkane (particularly pentane, hexane and heptane) and an aromatic, and similar products that are produced by the steps of: (a) refining a feedstock, (b) selectively removing hydrocarbons and (c) subsequently mixing the selected hydrocarbons, are not believed very effective in removing gummy layers of waxes and asphaltenes that are typically found in oil and gas reservoirs and well bores in relation to their cost. The waxy depositions in oil and gas formations are complex aggregations of molecules, with many layers and globules of different waxes and asphaltenes, which the inventors have found are not readily removed by simple compositions. Such products, requiring several processing steps, tend to be expensive. Also, in some wells such mixtures of an aromatic, alkane and alcohol

or other polar substance may increase the precipitation of waxes and asphaltenes. Thus for example, in the general case, stabilized C₅+ condensates tend to precipitate asphaltenes, with the future risk of wax contamination for the reasons just mentioned. That is to say, while it is possible to tailor a particular composition of alkanes and aromatics to a particular well formation, such a procedure is relatively expensive and may produce a product that is useful for one well formation but not for another. With the expense of the product and the risk of actually damaging the well, the application of such a product to a well is a venture not lightly undertaken.

The inventors have found a composition and a method for its use that helps to remove the uncertainty from applying wax solvating materials to wells, while at the same time significantly reducing the cost of making and using the composition. The composition is formed from a complex mixture of aromatics and alkanes (preferably C₇+). The complex mixture provides different components that solvate different waxes and asphaltenes. Rather than using a composition derived from selecting individual components during refining, the composition is the residue after lighter components (preferably substantially all C₁, C₂, C₃, C₄ and C₅) have been removed during refining. With the appropriate selection of the feedstock, an improved wax solvating and asphaltene solvating composition may be derived.

The feedstock should be selected to have a significant proportion of aromatics and alkanes. The inventors have found that if a feedstock has a mass percentage of trimethylbenzene higher than the mass

percentage of n-decane as determined by gas chromatography then the feedstock will have a sufficiently complex mixture of aromatics and alkanes for the efficient solvating of asphaltenes and waxes, particularly after the lighter ends (C₁, C₂, C₃, C₄ and C₅) have been removed by distillation from the feedstock. By a sufficiently complex mixture of aromatics is meant aromatics other than the simple aromatics benzene, toluene, ethylbenzene and xylene. These simple aromatics are the aromatics normally measured in gas chromatography since they usually yield well defined peaks. The inventors have found that it is necessary to have a good quantity of other aromatics, and the presence of these other aromatics is indicated by the quantity of trimethylbenzene.

Another indication that a feedstock contains a suitably complex blend of aromatics and alkanes to solvate complex gummy layers of waxes and asphaltenes is the presence of sulphur containing compounds in the feedstock. It is believed that sulphur is a catalyst for the conversion of alkanes to aromatics during the many years that the hydrocarbon deposit evolves underground. Hence, the more sulphur, the greater the conversion of alkanes to aromatics. Thus the presence of sulphur is an indication that the feedstock will have a suitable proportion of aromatics to alkanes.

Aromatic composition and alkane composition should be in the range 30% to 70% by mass percentage as determined by gas chromatography for a suitable composition. However, it is not believed that such a ratio of aromatics to alkanes is sufficient: the composition must be suitably complex as noted above. Further, it has been found desirable that the feedstock be clear or have a light colour such as

amber. Dark colour indicates the presence of heavy ends (C_{16}^+) that assist in the formation of waxes. The C_{16}^+ content of the fluid should preferably be below 2% by mass as determined by gas chromatography. If the feedstock contains greater than 2% C_{16}^+ content, then an additional cut may be taken to remove all or substantially all the higher ends.

Alternatively, the fluid may be formulated for pure asphaltene solvation. Pure asphaltene generally occurs in only two situations in the reservoir. In one case, pyrobitumen can be present in gas reservoirs. This is generally believed to have been deposited long ago when oil which had occupied the reservoir migrated out and left the pyrobitumen behind. This pyrobitumen can move during production and plug the formation or wellbore.

Another case is in tertiary recovery using hydrocarbon miscible solvents floods. Light hydrocarbons in the C_2 to C_5 range are injected into the reservoir to push the oil to production wells. While these light hydrocarbons will solvate paraffinic molecules they act to precipitate asphaltenic molecules. Thus asphaltene will precipitate without heavy paraffinic molecules present.

The fluid is formulated for solvating pure asphaltenes by increasing the temperature of the cutpoint. This removes the C_6 and C_7 components which contain a lower percentage of aromatics than the bulk residue. The aromatics in this region are small and not as effective as the more complex aromatics in the remainder of the fluid.

Asphaltenes are normally colloiddally suspended in crude oil by peptizing resins (maltenes). These peptizing resins are aromatic and polar at one

end and paraffinic or neutral at the other end. The polar end is attracted to the asphaltene and the nonpolar end to the crude oil. When the solid asphaltene is completely surrounded by peptizing resins it becomes a colloiddally suspended particule completely suspended in the crude oil.

Currently the main way of treating these precipitations is by injecting pure xylene down a well. Xylene is a simple aromatic with short paraffinic side chains. The more complex aromatics in the C₈+ fluid described here with longer side chains provide superior emulation of the maltenes that originally suspended the asphaltene molecules than just pure xylene.

BRIEF DESCRIPTION OF THE FIGURES

There will now be described preferred embodiments of the invention, with reference to the drawings, by way of illustration, in which like numerals denote like elements and in which Figs. 1 -4 are graphs showing gas chromatographic profiles of exemplary feedstocks for use in accordance with the invention. In each of Figs. 1 - 4, the relative peak heights of the components in the respective fluids are shown to illustrate the relative peak heights of trimethylbenzene and n-decane.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

As used in this patent document: a residual fluid is a fluid that remains after light components (particularly C₁, C₂, C₃, C₄ and C₅ components) of a hydrocarbon feedstock are removed during the refining of the hydrocarbon feedstock; a hydrocarbon feedstock is a hydrocarbon fluid that has been produced directly

from an oil or gas bearing formation; sour means sulphur containing. C_n+ indicates no greater than a small percentage (less than 5%) of C_1 , C_2 , ... C_{n-1} .

5 The preferred composition is a residual hydrocarbon fluid derived from a hydrocarbon feedstock having a complex mixture of aromatics. Complex in this context means that there are included in the mixture aromatics other than benzene, toluene, ethylbenzene and xylene, such as methylethylbenzene, diethylbenzene
10 and propylethylbenzene, to name but a few of the possibilities. The hydrocarbon feedstock from which the fluid according to the invention is derived should contain a greater percentage of trimethylbenzene than n-decane, in which case it is believed that the fluid
15 will have the desirable wax and asphaltene solvating properties. It should be noted that these aromatics, other than benzene, toluene, ethylbenzene and xylene, are not readily identifiable using gas chromatography, and so having the trimethylbenzene peak higher than n-
20 decane is the manner in which the appropriate feedstock may be identified. According to one aspect of the invention, the feedstock is preferably but not necessarily refined to remove essentially all C_1 , C_2 , C_3 , C_4 and C_5 components. It is not necessary that the
25 feedstock have a relatively low ratio of alkanes if the alkanes are concentrated in the lighter ends and the lighter ends are removed by distillation. The feedstock is preferably sour and clear or light amber, with sulphur content exceeding 1500 ppm, and
30 preferably has no more than about 2% $C_{16}+$. In general, it is believed that the more sulphonated the feedstock, the better for asphaltene solvation. If the $C_{16}+$ content is greater than 2%, a further cut should preferably be taken to remove the higher ends.

Figs. 1 and 2 are graphs of gas chromatographic profiles of compositions of feedstocks from which the fluid according to the invention may be derived. Fig. 1 is a gas chromatograph profile of the C₅+ feed from the Wildcat Hills plant in Alberta, Canada. Fig. 2 is a gas chromatograph profile of the C₅+ feed from the Jumping Pound plant in Alberta, Canada. The trimethylbenzene marker is indicated at 10 and the n-decane marker is indicated at 12 in each graph.

To produce the formulation of the invention from the feedstocks shown in Figs. 1 and 2, the feedstocks are refined to remove substantially all of the C₁, C₂, C₃, C₄ and C₅ components, with a small percentage of C₆, C₇ and C₈.

With a 120°C cut, the resulting fluid, as determined by gas chromatography, has about 0.1% pentane, 7% hexanes, 13% heptanes, 13% octanes, 7% nonanes, 9% decanes, 5% undecanes, 3% dodecanes, 2% tridecanes, 1% tetradecanes, 0.6% pentadecanes, 0.3% hexadecanes, 0.1% heptadecanes, 0.05% octadecanes, 1% benzene, 9% toluene, 12% ethyl benzene and meta- and para xylene, 2.6% ortho-xylene, 2.2% 1,2,4 trimethylbenzene, 0.1% cyclopentane, 2% methylcyclopentane, 2.6% cyclohexane, 8% methylcyclohexane and less than 0.05% of any other constituent, including cumulatively less than 0.1% C₁₉+. Naphthene content is greater than about 3%.

With a 130°C cut, the resulting fluid, as determined by gas chromatography, has about 0% pentanes, 2% hexanes, 13% heptanes, 13% octanes, 7% nonanes, 9% decanes, 5% undecanes, 3% dodecanes, 2% tridecanes, 1% tetradecanes, 0.5% pentadecanes, 0.2% hexadecanes, 0.1% heptadecanes, 0.05% octadecanes,

1.5% benzene, 12.6% toluene, 15% ethyl benzene and meta- and para xylene, 2.4% ortho-xylene, 2.2% 1,2,4 trimethylbenzene, 0% cyclopentanes, 1% methylcyclopentane, 1.9% cyclohexane, 7.8% methylcyclohexane and less than 0.05% of any other constituent, including cumulatively less than 0.1% C₁₉+. It will be observed that with the higher cut, all of the remaining pentane, and more than 2/3 of the hexanes have been removed while the aromatic content has increased.

With a 140°C cut, the resulting fluid, as determined by gas chromatography, has about 0% pentanes, 0.3% hexanes, 8.7% heptanes, 13.5% octanes, 6.7% nonanes, 10.7% decanes, 6% undecanes, 4% dodecanes, 2% tridecanes, 1% tetradecanes, 0.6% pentadecanes, 0.3% hexadecanes, 0.1% heptadecanes, 0.06% octadecanes, 0.6% benzene, 13.7% toluene, 17.9% ethyl benzene and meta- and para xylene, 2.7% ortho-xylene, 2.7% 1,2,4 trimethylbenzene, 0% cyclopentanes, 0.3% methylcyclopentane, 0.7% cyclohexane, 7% methylcyclohexane and less than 0.1% of any other constituent, including cumulatively less than 0.05% C₁₉+

With a 150°C cut, the resulting fluid, as determined by gas chromatography, has about 0% pentanes, 0.01% hexanes, 2.5% heptanes, 14.4% octanes, 9.5% nonanes, 14.1% decanes, 8.1% undecanes, 5.2% dodecanes, 3.1% tridecanes, 1.8% tetradecanes, 1% pentadecanes, 0.4% hexadecanes, 0.2% heptadecanes, 0.1% octadecanes, 0.01% benzene, 8.3% toluene, 20.3% ethyl benzene and meta- and para xylene, 3.5% ortho-xylene, 3.5% 1,2,4 trimethylbenzene, 0% cyclopentane, 0% methylcyclopentane, 0.07% cyclohexane, 3.7% methylcyclohexane and less than 0.05% of any other

constituent, including cumulatively less than 0.1% C₁₉⁺.

5 With a 160°C cut, the resulting fluid, as determined by gas chromatography, has about 0% pentanes, 0% hexanes, 0.2% heptanes, 7.9% octanes, 9.8% nonanes, 18.6% decanes, 10.8% undecanes, 6.9% dodecanes, 4.1% tridecanes, 2.3% tetradecanes, 1.2% pentadecanes, 0.5% hexadecanes, 0.2% heptadecanes, 0.1% octadecanes, 0% benzene, 2.2% toluene, 25.3% ethyl benzene and meta- and para xylene, 4.2% ortho-
10 xylene, 5.0% 1,2,4 trimethylbenzene, 0% cyclopentane, 0% methylcyclopentane, 0% cyclohexane, 0.5% methylcyclohexane and less than 0.05% of any other constituent, including an undetectable amount of C₁₉⁺.

15 For each of the 120°C, 130°C, 140°C, 150°C and 160°C cuts, all percentages are mass fraction. Only simple aromatics are identified. Supercritical fluid chromatography shows that the actual aromatic content is greater than 40%. For C₅ to C₁₈, the
20 percentage given is the sum of the peaks from the gas chromatographic analysis. Thus, the figure for "decanes" includes the figure for straight chain decane. The higher cuts show increased percentages of C₈ and C₁₀, and increased xylene, particularly the
25 150°C cut. The 130°C cut is preferred for wax and asphaltene solvation. For the 120°C cut, the fluid is amber in colour with a density of 780kg/m³. Boiling point at 1 atm is 100-300°C, freezing point about -60°C, vapour pressure <15kpa, with a closed cup flash point of >10°C. As a flammable and toxic liquid, this
30 fluid should be treated with well known safety precautions. At the higher cuts (150°C cut), effectively all of the C₆ and C₇ is removed, with

consequent increase in the xylene content to over 25%.
Such a fluid is useful for pure asphaltene solvation.

Thus a preferred composition of the invention has less than 1% cumulatively of methane,
5 ethane, propane, butane and pentane; 0 to 10% hexanes;
1 to 15% heptanes; 5 to 15% octanes; 5 to 15% nonanes;
5 to 15% decanes; 3 to 10% undecanes; 1 to 7%
dodecanes; 0 to 5% tridecanes; 0 to 3% tetradecanes;
0 to 2% pentadecanes; 0 to 1% hexadecanes; 0 to 1%
10 heptadecanes; 0 to 1% octadecanes; 0 to 3% benzene; 5
to 20% toluene; 10 to 35% xylenes; 1 to 5%
1,2,4trimethylbenzene; and cumulatively less than 2%
C₁₆+, all of the percentages being mass fraction as
determined by gas chromatography. In another preferred
15 composition according to the invention, the fluid
includes less than 5% hexanes; 0 to 15% heptanes; 0 to
15% octanes; 5 to 15% nonanes; 5 to 25% decanes; 3 to
15% undecanes; 2 to 10% dodecanes; 0 to 5% tridecanes;
0 to 3% tetradecanes; 0 to 2% pentadecanes; 0 to 1%
20 hexadecanes; 0 to 1% heptadecanes; 0 to 1%
octadecanes; 0 to 3% benzene; 5 to 15% toluene; 15 to
40% xylenes; and 1 to 8% 1,2,4trimethylbenzene.

Solvation tests using the formulation
according to the invention have yielded the following
25 results.

Table 1

No.	Location	Solvent	Contaminant	% <u>Dissolved</u>
30	1. 08-20-044-04W5	#8	1.0284	85.8
	2. 02-09-039-07	#8	0.9714	93.2
	3. 02-20-039-07	#8	0.9959	97.0
	4. 10-13 (Viking)	#8	1.0033	87.4
35	5. 06-10-035-06W4	#8	1.0280	95.2
	6. 10-13 (Viking)	#10	0.9972	63.2
	7. 06-10-035-06W4	#10	0.9547	64.2

13

	8.	10-24-001-26	#8	1.0005	71.7
	9.	8" Group Line	#8	1.0004	68.6
	10.	11-14-041-25	#8	1.0017	76.8
	11.	08-14-041-25	#8	1.0567	98.5
5	12.	11-14-041-25	#9	1.0011	81.1
	13.	08-14-041-25	#9	0.9987	97.2
	14.	Utikuma Keg R.	#8	0.9536	63.0
	15.	Utikuma Slave	#8	1.0221	98.2
	16.	Hutton 12-18	#8	1.0543	89.2
10	17.	10-18-048-08W5	#8	1.1200	97.8
	18.	12-24-047-09 W4	#16	0.9756	99.3
	19.	12C-19-036-04	#8	0.4624	87.3@22°C
	20.	16-01-004-21W3	#8	0.2992	75.2@22°C
	21.	Intensity Res.	#8	0.9845	97.1
15	22.	05-03-055-13W5	#8	0.9904	96.6
	23.	16-14-055-13W5	#8	1.0509	21.4
	23a.	16-14-055-13W5	Toluene	1.0458	* 38.1
	24.	Esso Wizard Lk.	90/10	0.9813	98.3
	25.	Esso Wizard Lk.	#8	0.9940	96.6
20	26.	Esso Wizard Lk.	Run 95	1.0018	91.3
	27.	Esso Wizard Lk.	90/10Xy	0.9726	97.0
	28.	Esso Wizard Lk.	100Xy	0.9676	96.5
	29.	16-03-040-04W5	#8	1.0485	84.5
	30.	16-03-040-04W5	#9	1.0264	96.1
25	31.	046-09W5 Comaplex	#8	1.0545	76.1
	32.	046-09W5 Comaplex	#9	0.9974	75.6
	33.	07-11-053-26	#8	1.0292	97.9
	34a.	16-19-071-04Chevron	#8	0.9756	94.4
	34b.	02-06-072-04Chevron	#8	1.0014	98.7
30	34c.	16-19-071-04Chevron	100Xylene	0.9588	95.7
	35.	02-06-072-04Chevron	100Xylene	1.4169	98.3
	36.	Chauvco Unit No. 2	#8	0.9799	97.6
	37.	06-10-035-03W5	#8	0.9548	66.5
	38.	08-20-026-12W4	#8	1.10157	92.2
35	39.	03-13-044-09Amoco	#8	1.0397	82.9
	40.	04-22-043-08Amoco	#8	0.9671	94.1
	41.	02-05-043-08Amoco	#8	1.0202	98.8
	42.	03-13-044-09Amoco	#9	0.9975	72.5
	43.	04-22-043-08Amoco	#9	0.9760	96.1
40	44.	02-05-043-08Amoco	#9	1.0372	95.3
	45.	Willesden Green	#8	1.0127	94.1

Notes to Table 1: Wax or asphaltene amount is listed in grams under the heading "contaminant". The sample is indicated by the location of the well, in the Province of Alberta, Canada, from which the sample was derived. % dissolved is the percentage of the original sample that was dissolved in the solvent.

It is a general indicator of the effectiveness of the solvent on that particular composition of contaminant. The amount of solvent used was 100mL. #8 and #16 is the fluid described above as the 120°C cut. #9 is a
5 blend of NP760tm and 10% Super A Soltm, which is available from Wellchem of Calgary, Alberta, Canada. #10 is Petro Rep condensate having about 15% butanes, 46% pentanes, 19% hexanes and less than 1% aromatics as determined by gas chromatography. Run 95 is 100%
10 FRACSOL well site operation fluid available from Trysol Limited, of Calgary, Alberta. 90/10 is 90% of the 120°C cut with 10% of a non-aromatic brominated non-fluorinated hydrocarbon such as dibromomethane. 90/10Xy is 90% of the 150°C cut described above with
15 10% of a non-aromatic brominated non-fluorinated hydrocarbon such as dibromomethane. 100Xy is 100% of the 150°C cut described above. 100Xylene is pure xylene. Toluene is pure toluene. The oils from which some of the contaminants precipitated so far as known
20 have the following composition: Sample 1. 8.26% asphaltene, 11.2% wax; Sample 4. 10% asphaltene; Sample 5. 23% asphaltene; Sample 22. 1.11% asphaltene, 4.7% wax; Sample 34c. 6.12% asphaltene, 2.9% wax; Sample 36. 3.43% asphaltene, 3.8% wax.

25 These results show that the formulation of the present invention provides comparable solvation properties to highly refined and expensive wax solvation products when applied to a variety of wells without specifically formulating the composition to
30 the well formation.

By comparison with the product of the present invention, so far as known, the condensate available from other gas plants located in the Province of Alberta is not desirable for use as a wax

and asphaltene removing fluid. Thus, for condensate from Amerada Hess (Bearberry), while the fluid is clear, showing low heavy ends, the aromatic content is too low by comparison with the light ends for a useful feedstock. Condensate from the Can-Oxy Mazeppa plant is dark red from the plant, which becomes black when the lighter ends are removed, that is, when a C₇+ cut is taken, thus indicating the presence of undesirable heavy ends. Condensate from the Burnt Timber plant has too many heavy ends to work as a solvent, but may be formation compatible in some wells. Condensate from the Brazeau plant has too few aromatics, and too many waxes to be useful as a solvent. Condensate from Mobil Oil Lone Pine Creek has 6% xylene, which might suggest it is similar to the Jumping Pound feed (6.5% xylene). However, the relative lower percentage of lighter ends means that the concentration of xylene and other aromatics does not increase greatly if the lighter ends are removed in accordance with the principles of the invention. Consequently, the feed is not very useful as a solvent. Condensate from the Husky Oil Ram River plant has too many heavy ends, as indicated by its dark colour, and has too few aromatics to make it a useful feed for a solvent.

In the method of the invention, a C₅+ hydrocarbon feedstock is obtained in which feedstock the mass percentage of trimethylbenzene exceeds the mass percentage of decane as determined by gas chromatography; and substantially all hydrocarbons having 1, 2, 3, 4 and 5 carbon atoms are removed, thereby producing a residual fluid, effectively a C₇+ fluid. The fluid is applied to a well as follows.

For pumping or flowing wells, the well should be de-waxed before attempting to clean up the

formation. To clean a pumping well, an amount of the fluid of the invention equal to about one half of the tubing volume should be circulated in the well with a bottomhole pump for about 24 hours. To clean the nearby well bore formation, a squeeze volume (1.0 - 1.5 m³ per meter of perforations) of the fluid according to the invention should be squeezed into the formation with a clean, formation compatible fluid. Preferably, the displacement fluid should be filtered to remove fines. After the fluid has been squeezed into the formation, the well should be shut in, and the fluid allowed to stand for 12 hours before putting the well back on pump.

To clean a partially plugged flowing well, a volume of the fluid according to the invention equal to one half of the tubing volume should be injected down the tubing string and allowed to soak for 24 hours. The well may then be placed back on production and tested.

To clean a completely plugged well, an attempt should be made to solubilize the plug by injecting a volume of the fluid according to the invention down the tubing string. If the plug can be solubilized, then the well should be allowed to soak for 24 hours and the well may be placed back on production and tested. If the plug cannot be solubilized, then the plug may be removed by such procedures as drilling or jetting with coiled tubing, using the fluid according to the invention as the jetting fluid. The well may then be placed back on production and evaluated.

To squeeze a flowing well in which the tubing is set in a packer, it is preferred to inject the fluid according to the invention directly through

the perforations into the well bore using coiled tubing. This helps to prevent well fluid entrained solids from being re-injected into the well. If this procedure is not viable, then an attempt may be made to force the fluid according to the invention through the tubing into the formation with a clean formation compatible chase fluid. Care should be taken not to overflush the chase fluid into the formation.

To squeeze a flowing well in which the tubing is not set in a packer, it is preferred to squeeze a squeeze volume of the fluid according to the invention down the annulus to the perforations. The flowline should be kept open until the resident annulus fluid has been displaced up the tubing into the flowline. Typical squeeze volumes are 1.0 - 1.5 m³ of the fluid according to the invention per meter of perforations. Once the fluid is in the annulus, the tubing valve may be closed and the fluid squeezed into the formation with a clean formation compatible fluid (which should not be overflushed). In either case (with or without the tubing set in a packer), the well may be shut in, allowed to soak and after 24 hours or so, placed back on production and tested.

If a flowing well does not flow after treatment, it may be desirable at that point to swab the well.

The formulation of the present invention, identified by Trysol Limited's trademark WAXSOL is preferably pumped into the well at below fracturing pressures. Pumping is carried out at ambient temperature. As known in the art, since the formulation of the invention is aromatic rich, contact with elastomeric components in the well should be minimized. For removal of the formulation of the

invention from the well, high (maximum) pump speeds are recommended to aid in preventing the plugging of downhole pumps by release of fines and scale from downhole wax as it is dissolved.

5 Further feedstocks include the Shell
Caroline condensate available from the Shell Caroline
gas plant at Caroline, Alberta, Canada. A gas
chromatograph profile of the feedstock is shown in
Fig. 3, with the TMB peak shown at 10 and the n-decane
10 peak shown at 12. Composition of the feedstock, as
determined by gas chromatography, is about as follows
(all percentages are mass percentage): 0% C₁-C₅, 3.8%
n-hexanes, 7.4% octanes, 7.4% heptanes, 3.1% nonanes,
10.1% decanes, 5.2% undecanes, 2.6% dodecanes, 1.4%
15 tridecanes, 1.05% tetradecanes, 1.1% pentadecanes,
1.05% hexadecanes, 1% heptadecanes, 2.5% octadecanes;
2.85% nonadecanes, 0.5 eicosanes, 0.1% heneicosanes,
0.01 % docosanes, 0.5% benzene, 9.7% toluene, 26.3%
xylenes, 5.7% 1,2,4-trimethylbenzene, 1%
20 methylcyclopentane, 1.2% cyclohexane and 4.4%
methylcyclohexane, although total aromatic content
including more complex aromatics have been analyzed by
supercritical fluid chromatography at greater than 40%
mole fraction.

25 A further feedstock, perhaps the most
preferred for its wax solvating capabilities, is shown
in the gas chromatograph profile shown in Fig. 4, with
the TMB peak shown at 10 and the n-decane peak shown
at 12. This feedstock is from the Hanlan gas plant in
30 Alberta, Canada.

A xylene rich composition according to the
invention, namely a composition with greater than 25%
mass percentage xylene as determined by gas
chromatography, and preferably greater than about 70%

aromatics (actual mass percentage as determined by mass spectrometry), as for example derived from the feedstock illustrated in Fig. 2 with the cut at above 150°C, or the feedstock illustrated in Fig. 4 with the cut at above 145°C, is known as XYSOL¹ fluid. A mixture of XYSOL¹ fluid with gasoline (Shell BronzeTM) or other similar hydrocarbon fluid composed primarily of alkanes in a 40/60 ratio (40% XYSOL¹ fluid and 60% gasoline) also provides a suitable wax solvating formulation while preventing the precipitation of asphaltenes. Composition of the mixture, as determined by gas chromatography, is about as follows (all percentages are mass percentage): 0% methane and ethane, 0.01% propane, 0.77% isobutane, 6% normal butane, 4.60% isopentane, 3.78 normal pentane, 6.1% hexanes, 7.6% heptanes, 4.6% octanes, 3% nonanes, 6% decanes, 15% undecanes, 5% dodecanes, 3% tridecanes, 2% tetradecanes, 1% pentadecanes, 1% hexadecanes, less than 1% C₁₇+, 0.9% benzene, 7.8% toluene, 15.2% xylenes, 2.2% 1,2,4-trimethylbenzene, 3.6% cyclopentane, 1.4% methylcyclopentane, 0.3% cyclohexane and 0.7% methylcyclohexane.

Such a formulation combines the wax solvating capabilities of the invention with the low cost of the gasoline and provides an inexpensive wax solvating composition. The gasoline is selected for its low cost and relatively low percentage (<2%) of C¹⁶+ fluid, and may contain impurities commonly found in gasoline such as oxidative inhibitors, corrosion inhibitors and inductive system detergents. The proportion of xylene rich composition to gasoline that will make a suitable wax solvating composition depends

¹XYSOL is a trademark of Trysol Limited, Alberta, Canada.

on the respective aromatic content of the gasoline and the xylene rich composition, and the resulting mixture should have at least 30% aromatics as determined by gas chromatography. Gasoline is a volatile flammable hydrocarbon fluid that includes predominantly alkanes in the C₄ - C₁₂ range.

Such a composition is made by selecting a hydrocarbon feedstock containing xylene and in which the mass percentage of trimethylbenzene exceeds the mass percentage of n-decane as determined by gas chromatography, refining the feedstock to increase the xylene content to above 25% as determined by gas chromatography to produce a xylene rich composition; and mixing the xylene rich composition with an amount of gasoline such that the aromatic content of the resulting fluid is greater than 30% as determined by gas chromatography.

A person skilled in the art could make immaterial modifications to the invention described and claimed in this patent without departing from the essence of the invention.

7. A method of producing a wax and asphaltene solvating oil well site operation fluid comprising the steps of:

obtaining a hydrocarbon feedstock;

5 performing a gas chromatographic analysis on the feedstock to determine whether the mass percentage of trimethylbenzene exceeds the mass percentage of n-decane; and

10 if the mass percentage of trimethylbenzene exceeds the mass percentage of n-decane, then subsequently applying the feedstock or a derivative of the feedstock to a well having wax-like contaminants.

8. The method of claim 7 further including removing substantially all hydrocarbons having 1, 2, 3, 4 and 5 carbon atoms from the feedstock, thereby producing a residual fluid.

9. The method of claim 7 in which the feedstock or a derivative of the feedstock is allowed to stand in the well.

10. The method of claim 7 further including recovering the feedstock or derivative of the feedstock from the well.

11. The method of claim 7 further comprising: removing substantially all hydrocarbons having 6 or 7 carbon atoms.

30

12. The method of claim 7 further comprising: refining the fluid to reduce C₁₆+ content.

13. A method of making an oil and gas well operation fluid comprising the steps of:

5 selecting a hydrocarbon feedstock containing xylene and in which the mass percentage of trimethylbenzene exceeds the mass percentage of n-decane as determined by gas chromatography;

10 refining the feedstock to increase the xylene content to above 25% as determined by gas chromatography to produce a xylene rich composition; and

15 mixing the xylene rich composition with an amount of gasoline to produce a resulting fluid such that the aromatic content of the resulting fluid is greater than 30% as determined by gas chromatography.

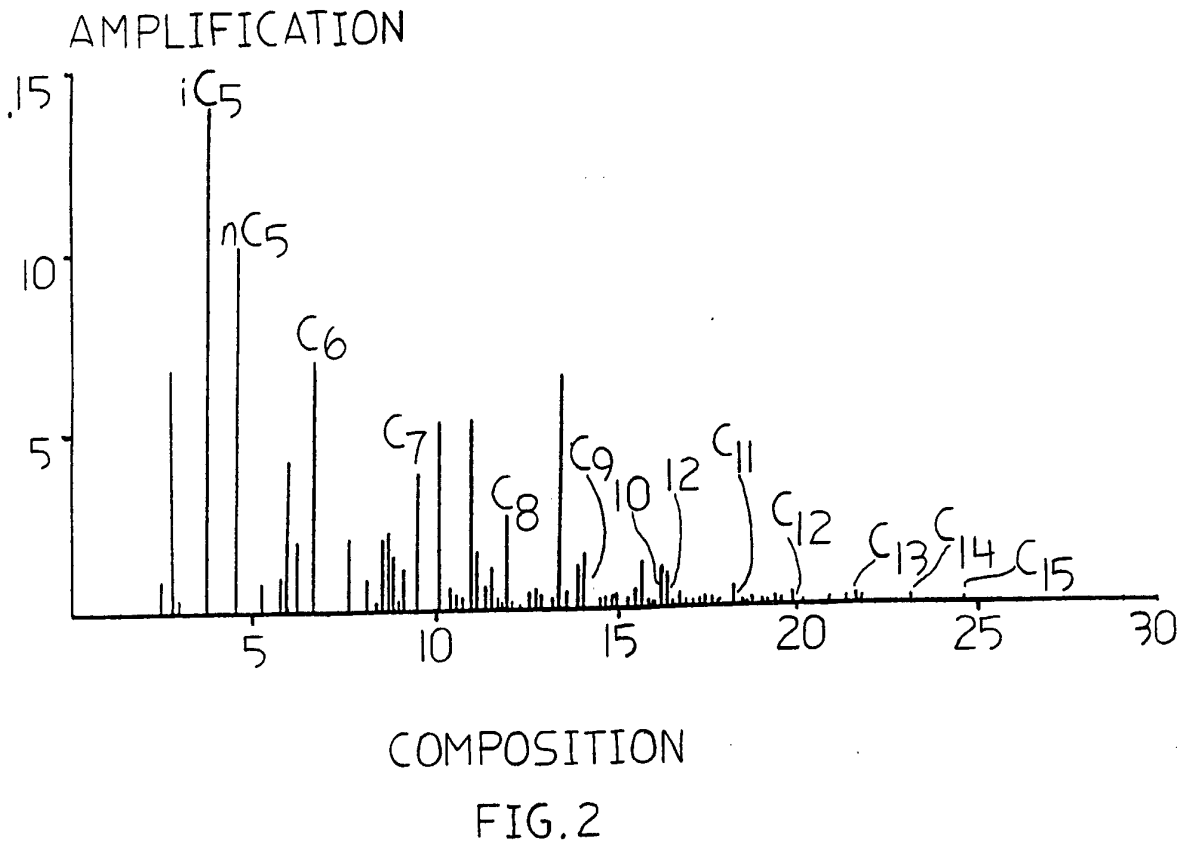
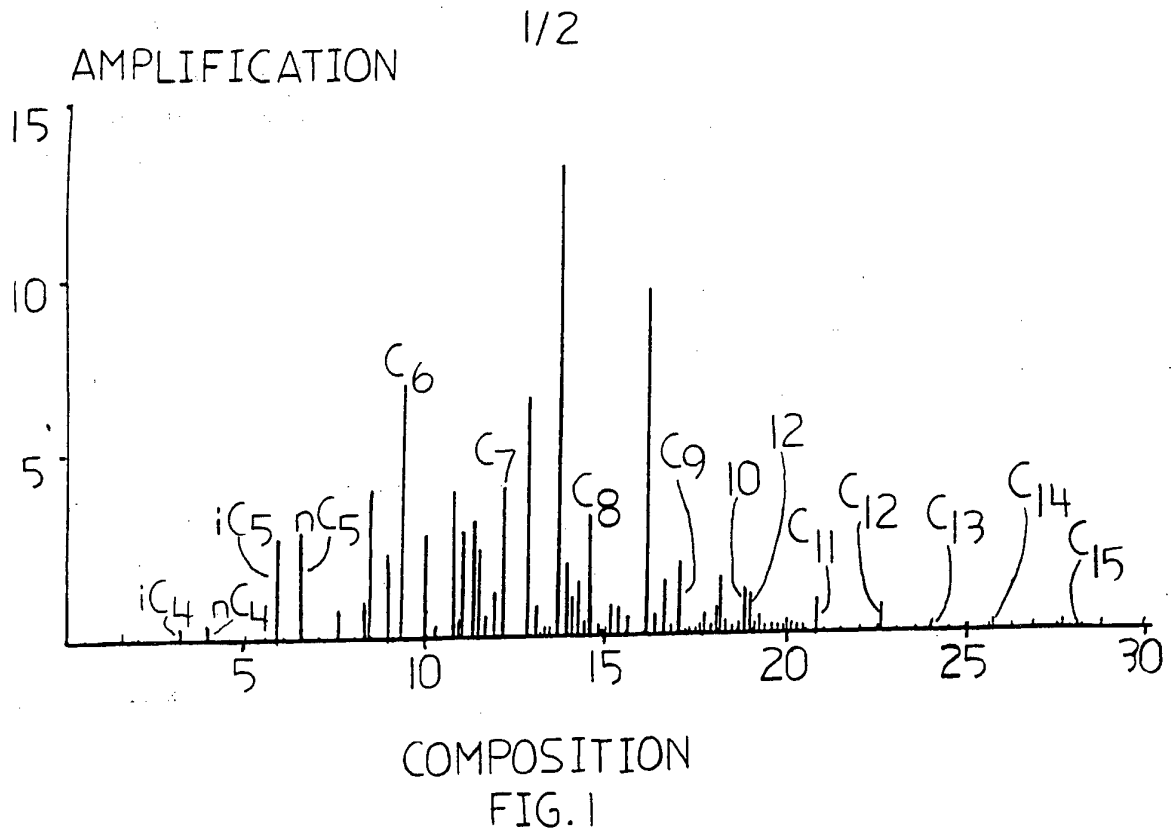
14. The method of claim 13 further including applying the resulting fluid to an oil or gas well.

20 15. The method of claim 14 in which the resulting fluid is allowed to stand in the well.

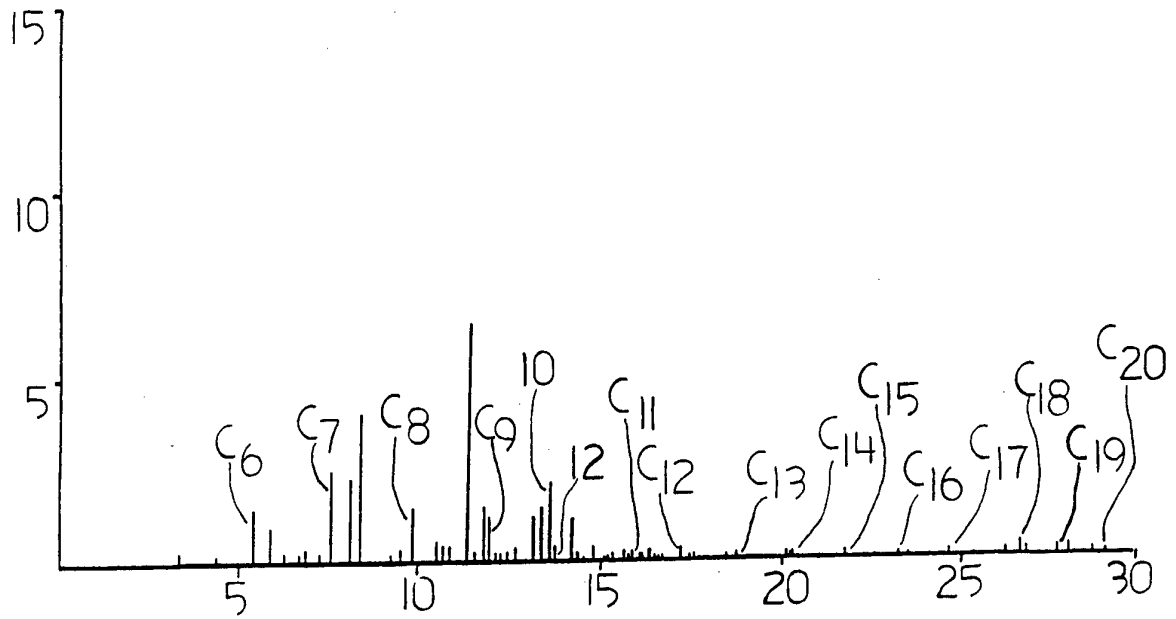
16. The method of claim 15 further including recovering the resulting fluid from the well.

25 17. The method of claim 13 further comprising: removing substantially all hydrocarbons having 6 or 7 carbon atoms from the feedstock during refining.

30 18. The method of claim 13 further comprising: refining the fluid to reduce C₁₆+ content of the fluid.

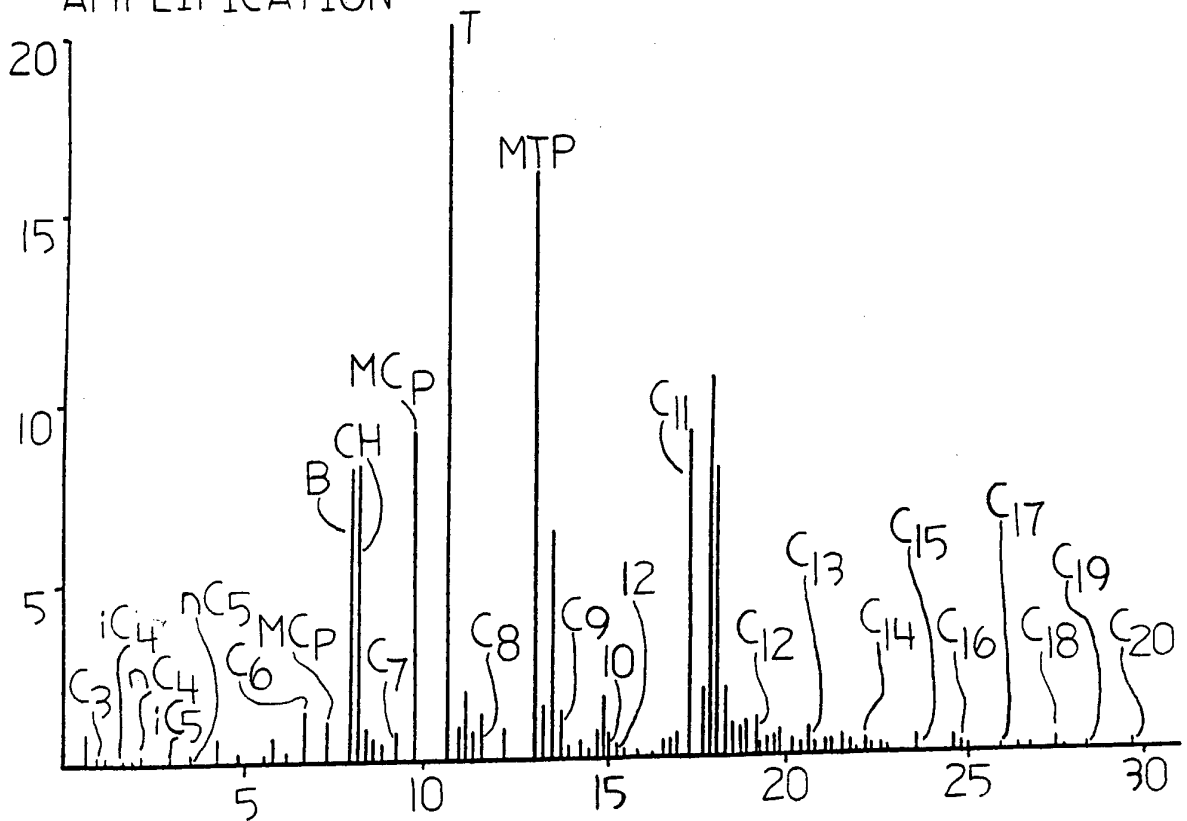


AMPLIFICATION



COMPOSITION
FIG. 3

AMPLIFICATION



COMPOSITION
FIG. 4