

Monitoring of the Content of Imidazoline-Containing Corrosion Inhibitor

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(Received December 02, 2016; Revised December 02, 2016; Accepted August 03, 2017)

The qualitative composition of active components of the corrosion inhibitor CGW-85567 was studied. It was found that C18:2 and C18:1 imidazolines and the corresponding imidazolin-amides are the major components. The HPLC/MS technique was developed for their determination in the water solutions of monoethylene glycol (MEG). Industrial application of the inhibitor showed that MEG solution retained high concentration of the inhibitor for a long time after ceasing its addition into pipelines. Low values of the partition coefficients (0.010-0.014) of imidazolines in the system “water solution of MEG (concentration of MEG 62-85% v/v) - gas condensate” have allowed to pass on from the technology of continuous pumping of the inhibitor into protected pipelines to the periodic dosing technology. Taking into account a long time of circulation in the system and high temperatures during MEG regeneration process possible degradation products of the inhibitor were studied. N, N-dimethyl-dodecanamine-1, and N, N-dimethyl-tetradecanamine-1 were identified as major degradation products of the corrosion inhibitor CGW-85567.

Keywords: corrosion inhibitor, imidazoline, HPLC/MS, tertiary amines, monoethylene glycol

1. Introduction

With the very beginning of field development of deep-laying gas condensate deposits when pressure head sealed systems excluding significant amounts oxygen of air began to be applied, carbon dioxide became the main corrosion component of the gas phase. Accumulation of condensed water in the coupling gaps of tubing led to their fast corrosion destruction [1]. Therefore various corrosion inhibitors began to apply in such systems. The widespread substances used as corrosion inhibitors are imidazolines. They are cationic surface-active substances with a positive charge on imidazoline core. Their film-forming properties allow using them as corrosion inhibitors.

Usually imidazoline molecule consists of so-called “head” – imidazoline core, “pendant” and hydrocarbon “tail”. Molecular modeling shows; that the “head” and the pendant are charged with adsorption of the molecule on a surface, and the hydrocarbonic “tail” forms a protective monolayer [2,3].

In this paper we will consider application of the corrosion inhibitor in carbon steel multiphase pipelines which transport gas-liquid mixture of natural gas, gas condensate, and water solution of monoethylene glycol (MEG). A pro-

gram of corrosion protection and monitoring has been developed to assure specified lifetime of the pipelines. Application of a corrosion inhibitor is a part of the program. Corrosion inhibitor should reduce corrosion rate in water solution of MEG to less than 0.1 mm per year and should be long-term temperature stable at 140 °C (temperature of MEG regeneration). As a result of intensive laboratory studies corrosion inhibitor CGW-85567 manufactured by Baker Petrolite Company has been selected. According to the laboratory data it provides necessary corrosion rate at concentration 25 mg/dm³.

The widespread method of measurement of the corrosion inhibitor concentration in water phase is based on the formation of coloured complex by nitrogen-contained compounds and methyl orange in the acid medium [4]. This method gave incorrect results in our case. Preliminary laboratory tests showed that this method led to the over-estimation of the corrosion inhibitor concentration at 5-15 times. Probably, under high-temperature conditions in the MEG regeneration system some substances that are also form complexes with methyl orange are formed.

The aims of our work were determination of qualitative composition of CGW-85567 corrosion inhibitor and selection the conditions for HPLC analysis of its imidazoline components for the monitoring CGW-85567 concentration in the pipelines. Additionally, we have tried to reveal pos-

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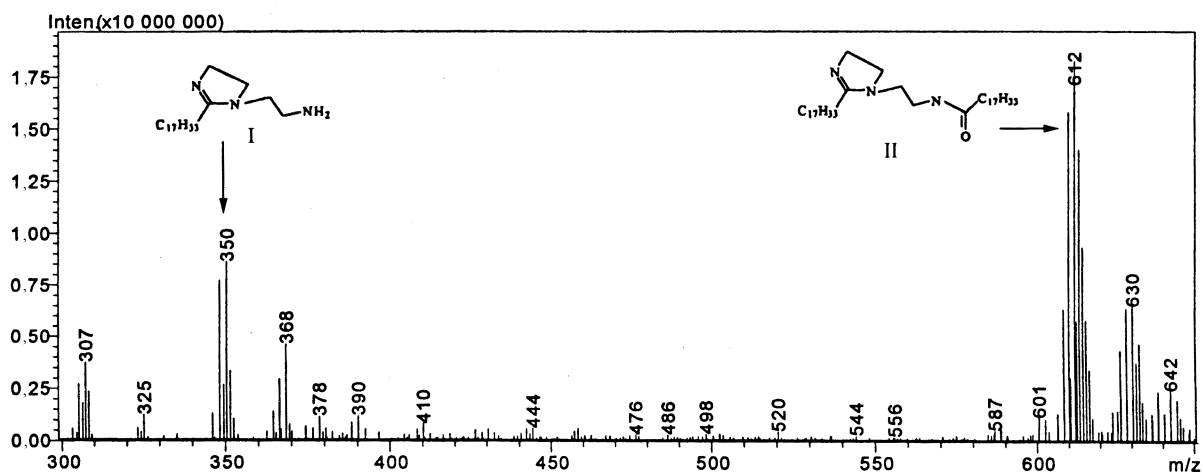


Fig. 1 Mass-spectrum of CGW-85567 corrosion inhibitor (ESI +, direct infusion).

sible degradation products of the CGW-85567 and evaluate their concentration.

2. Experimental Procedure

According to the manufacturer CGW-85567 contains 30 - 60% of MEG, from 10 to 30% of imidazoline salts, and 1 - 5% of mercaptoethanol.

The CGW-85567 mass spectra were taken with the mass selective detector Shimadzu LCMS-2010EV, source ESI, registration of positive ions. HPLC/MS separations were carried out with liquid chromatograph Shimadzu LC-20A, reversed-phase column Dionex Acclaim Surfactant (ODS, 4.6 mm I.D. x 150 mm, 5 μ m) was used, eluent rate was 0.8 mL/min. A splitter was mounted after column so one third of eluate went to the mass-selective detector. Separations were carried out in gradient of acetonitrile - water, with the addition of ammonium acetate titrated with acetic acid to pH 4.0. Concentration of acetate in mobile phase was 0.01 M and did not change during analysis. Initial concentration of acetonitrile was 25%, 0-10 min - linear gradient to 40%, 10-25 min - isocratic segment, 25-36 min - linear gradient to 90% of acetonitrile. For quantitative analysis samples were diluted with equal volume of isopropanol.

For the identification of CGW-85567 degradation products GLC-MS method was used. Analyses were carried out with an instrument Shimadzu GCMS-QP 2010 equipped with the pyrolyser PY-2020iD adjusted on simple evaporation of liquid sample at 250 $^{\circ}$ C. The column Ultra ALLOY-5 was used for separations under temperature programming from 40 $^{\circ}$ C (initial duration 3 min) to 320 $^{\circ}$ C, rate 20 $^{\circ}$ C/min, gas-carrier - helium, 1 mL/min, splitter

1:200. The temperature of MS-interface was 280 $^{\circ}$ C, ion source - 250 $^{\circ}$ C, detector voltage 1.1 kV. Mass spectrum libraries NIST 08 and Wiley 8 were used for identification.

For quantitation of tertiary amines in the water solutions of MEG Shimadzu GC-2010Plus chromatograph with thermoionic detector FTD-2010 Plus and injector with programming of temperature OCI/PTV-2010 were used. Separations were carried out with the column SGE SolGel-1MS (30 m \times of 0.25 mm I.D., phase of 0.25 μ m) under temperature programming from 100 $^{\circ}$ C (initial duration 1 min) to 300 $^{\circ}$ C, rate 20 $^{\circ}$ C/min, gas-carrier - helium, linear rate - 40 sm/sec, splitter 1:40. Temperature program of the injector: initial temperature 200 $^{\circ}$ C (30 s) then heating to 350 $^{\circ}$ C with the rate 100 $^{\circ}$ C/min. Temperature of detector FTD was 350 FTD, current 3 pA.

3. Results and Discussion

The CGW-85567 mass spectrum is shown on Fig. 1. Intensive signals with m/z 348 and 350 were ascribed to C18:2 and C18:1 imidazolines respectively; signals with m/z around 610-614 - to the corresponding imidazolin-amides. Presence of these components may be related to the conditions of synthesis of imidazolines. If major components of raw material are oleic acid and diethylenetriamine at molar ratio 1 : 1 then C18:1 imidazoline is formed. At molar ratio of oleic acid - diethylenetriamine 2 : 1 C18:1 imidazoline-amide is formed [5]. Signals with m/z bigger on 18 units (368 and 630) are presumably ascribed to amide-amines that are the predecessors of imidazolines or imidazoline-amides at the synthesis.

For an effective application of the corrosion inhibitor it is necessary to control its concentration in the protected

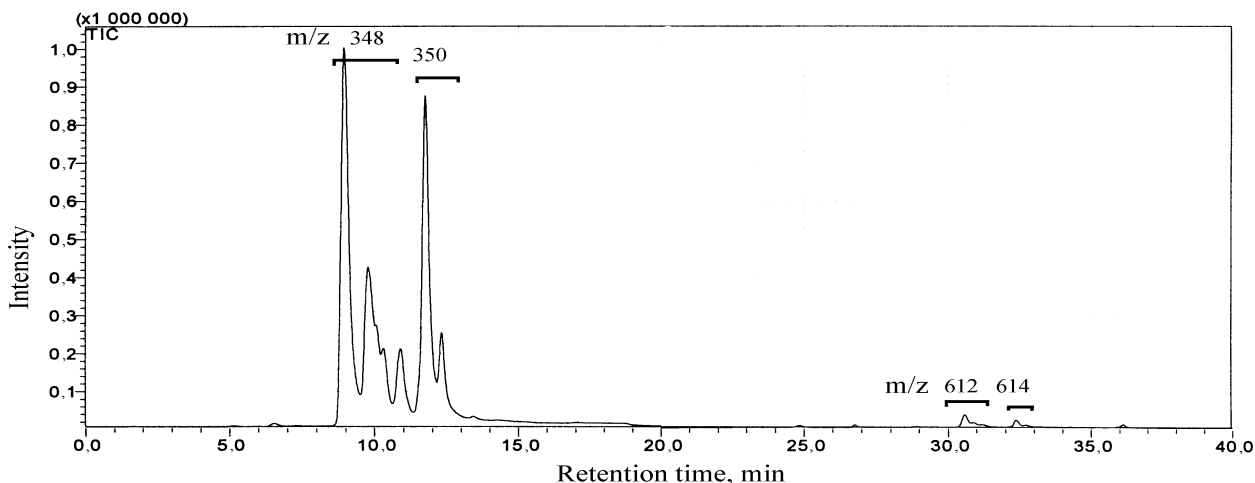


Fig. 2 Chromatogram of CGW-85567 corrosion inhibitor (concentration 10.6 mg/l). SIM 348, 350 (20 min), 612, 614 (20-40 min).

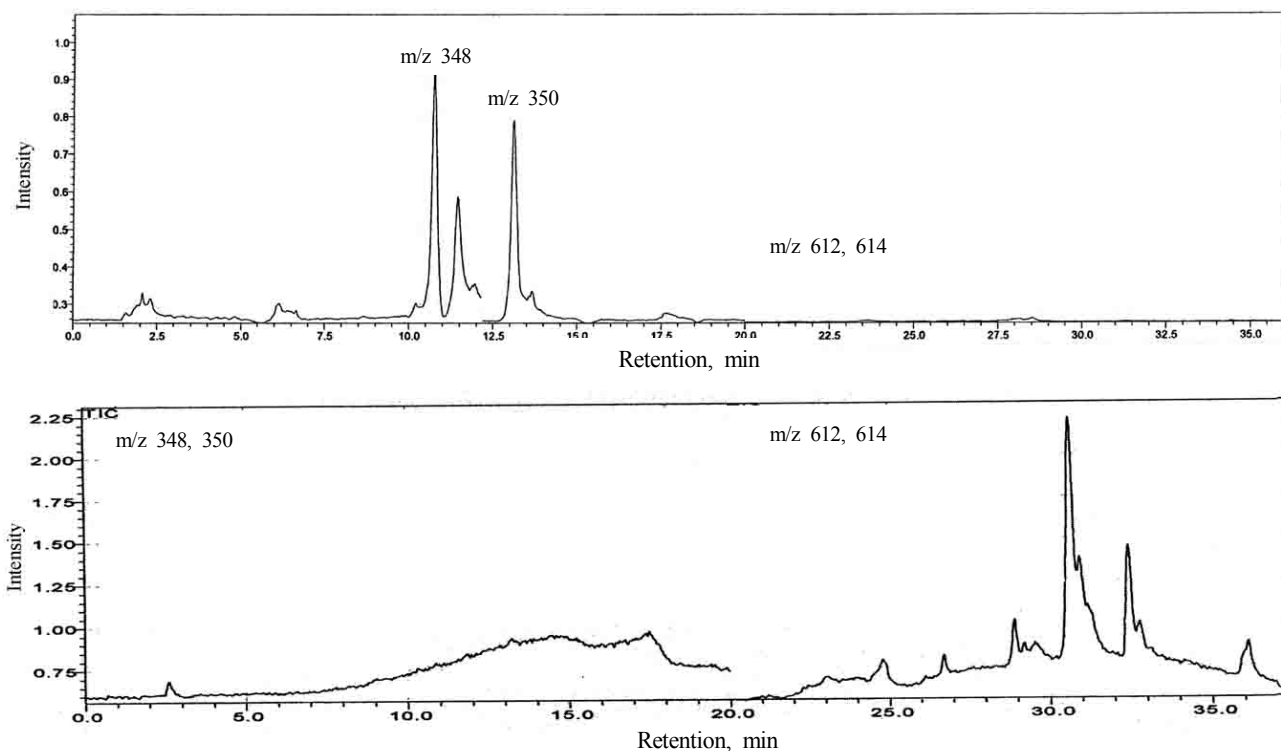


Fig. 3 Chromatogram MEG solution sample taken from multiphase pipeline (upper chromatogram) and sample of gas condensate (lower chromatogram).

system. HPLC can be successfully used for this purpose [2,5-7]. Main difficulties can be caused by the presence in the sample both alkyimidazolines and alkyimidazoline-amides which are considerably different in the physical and chemical properties and therefore in the chromatographic mobility. For their separation number of phases and columns has been tested at various pH and mobile phases. Separation of alkyimidazoline-amides can be

reached on various phases (for example, ODS, -NH₂) at pH acetate buffer at pH 4.75 and above however resolution of alkyimidazolines is insufficient; their peaks have tails that causes problem for the quantitative analysis. Decrease of mobile phase pH to 4.0 leads to considerable improvement of peak form. Fig. 2 shows chromatogram of CGW-85567 corrosion inhibitor. Presence of peaks with the same m/z may be explained by cis-trans isomer-

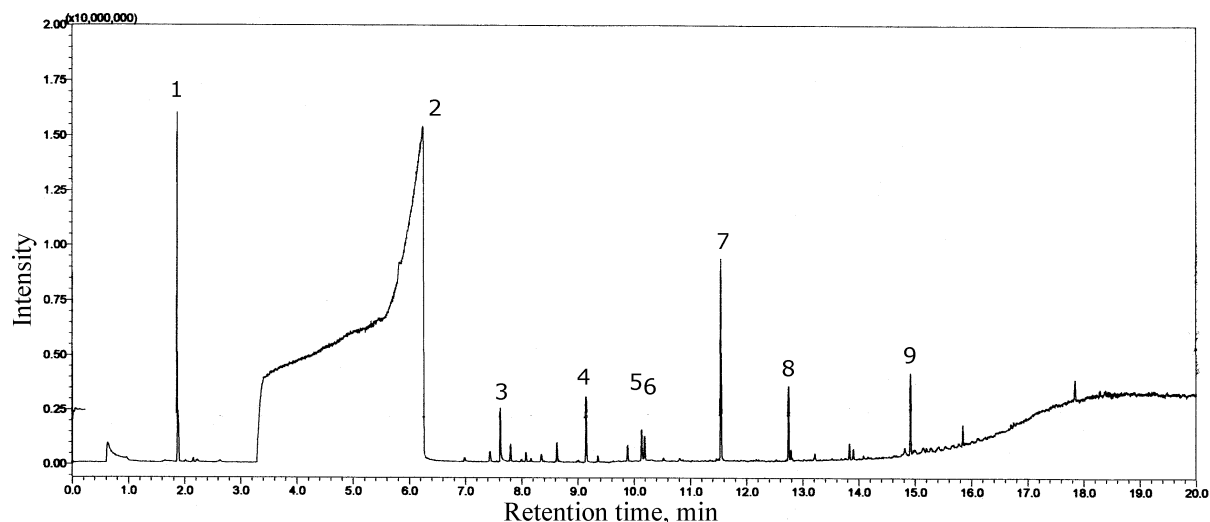


Fig. 4 GLC/MS-chromatogram of MEG solution from pipeline taken after separation of gas condensate. 1-isopropanol, 2-MEG, 3 - diethyleneglycol (coincidence to library spectrum of 97%), 4 - benzylacetate (96%), 5 - benzyl ether of ethyleneglycol (94%), 6 - N, N-dimethyldodecanamine-1 ($C_{12}H_{27}N$) (95%), 7-N, N-dimethyldodecanamine-1 ($C_{14}H_{31}N$) (98%), 8-N, N-dimethyltetradecanamine-1 ($C_{16}H_{35}N$) (97%), 9 - N-methyl-N-benzyl-dodecanamine-1 ($C_{20}H_{35}N$) (97%).

isation of fatty acids in the imidazolines synthesis process. Achieved separation is sufficient for the quantitative analysis of active component of CGW-85567 in the MEG samples.

The chromatogram of the MEG water solution sample taken from the multiphase pipeline protected with CGW-85567 is shown on Fig. 3. For the quantitative analysis we tested two methods: calibration curve and standard addition. Latter one gave better results in terms of reproducibility and stability that possibly may be related to complex matrix of the samples including inorganic salts, MEG, and hydrocarbons.

Industrial application of the inhibitor showed that, in spite of initial supposition that the most part of the inhibitor would leave system in a short time with condensate, MEG solution retained high concentration of the inhibitor for a long time after ceasing its addition into pipelines. Study of gas condensate samples has shown (Fig. 3, lower chromatogram) that non-polar organic phase contained mainly imidazoline-amides; while imidazolines were retained with solution water-MEG.

In laboratory conditions with described above HPLC/MS technique we have determined partition coefficient L for one of major components of studied inhibitor (imidazoline C18:2, m/z 348) in systems "water solution of MEG – condensate" and "mineralized water – condensate":

$$L = \frac{C_{cond}}{C_{MEG}}$$

where c_{cond} - concentration of imidazoline C18:2 in condensate, c_{MEG} - concentration of imidazoline C18:2 in solution of MEG. Values of L were 0.010 - 0.014 and more than 3; respectively. Low values of partition coefficient in system "water solution of MEG – condensate" has allowed to pass on from the technology of continuous pumping of the inhibitor into protected pipelines to the periodic dosing technology. Average periodicity of dosing (usually 1-2 times a month) and quantity of the inhibitor dosed (usually about 500 l) can be corrected according to the monitoring of the inhibitor residual concentration and corrosion rate.

Taking into account a long time of circulation of the corrosion inhibitor in the system and high temperatures during MEG regeneration process we studied possible degradation products of the corrosion inhibitor. Solutions of MEG after separation of gas condensate were taken for analysis and 8 major peaks were identified with GLC/MS method (Fig. 4). Considering chemical structures of imidazolines, decomposition products of the corrosion inhibitor can be tertiary amines - N, N-dimethyldodecanamine-1, N, N-dimethyl-dodecanamine-1, N, N-dimethyltetradecanamine-1, N-methyl-N-benzyl-dodecanamine-1. These substances have been found neither in pure corrosion inhibitor nor in pure MEG solution.

For quantitative analysis of tertiary amines highly selective thermoionic (nitrogen-phosphorus) detector was used which was not sensitive to hydrocarbons. N, N-dimethyloctylamine was used as internal standard. Chromatogram of MEG solution from pipeline taken after separation of

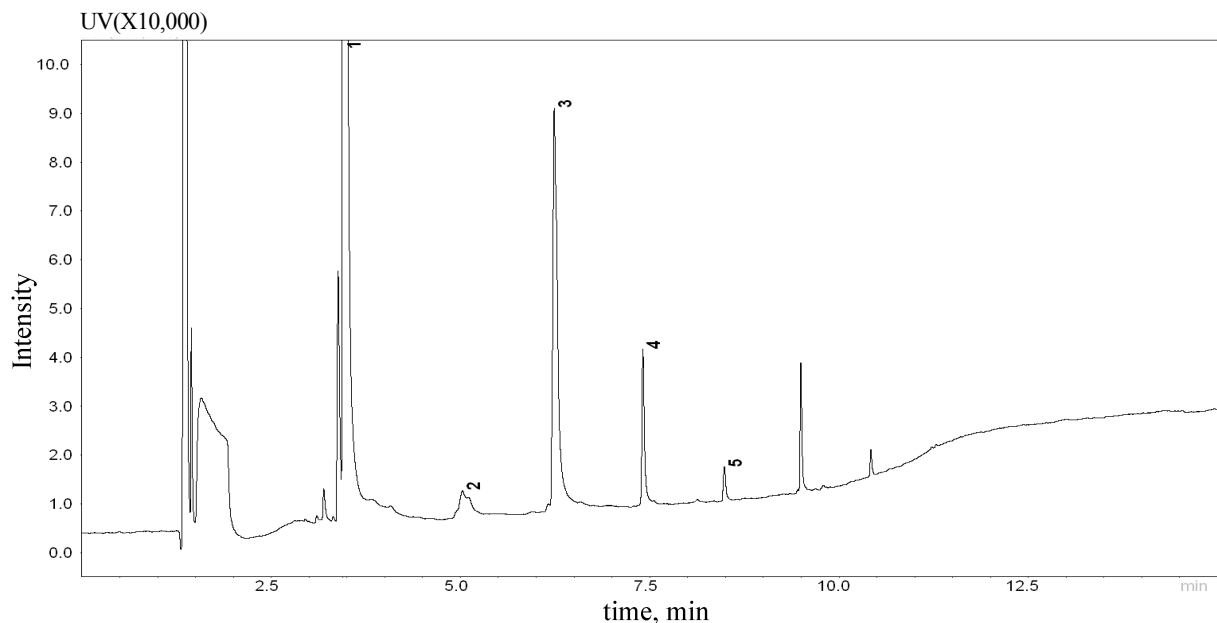


Fig. 5 GLC-chromatogram of MEG solution from pipeline taken after separation of gas condensate. 1 - internal standard N, N-dimethyloctylamine, 2 - N, N-Dimethyldecanamine, 3 - N, N-dimethyldodecanamine, 4 - N, N-Dimethyltetradecanamine, 5 – N-benzyl-N-methyldodecanamine.

Table 1 Content of tertiary amines at in MEG solution

Sample point	Concentration, mg/l			
	N,N-Dimethyl-decanamine	N,N-dimethyl-dodecanamine	N,N-Dimethyl-tetradecanamine	N-benzyl-N-methyl-dodecanamine
Before separation MEG and gas condensate 10.04.2013	0.7±0.1	17.5±1.3	4.9±0.5	0.9±0.1
Before separation MEG and gas condensate 17.04.2013	1.6±0.2	23.8±2.8	7.0±0.4	1.2±0.1
After separation MEG and gas condensate 10.04.2013	1.3±0.2	37.9±4.1	8.3±0.4	1.8±0.2
After separation MEG and gas condensate 17.04.2013	0.6±0.1	24.2±3.2	6.3±0.3	1.1±0.1
MEG after regeneration 10.04.2013	0.7±0.1	42.9±3.5	8.6±0.4	1.8±0.2
MEG after regeneration 17.04.2013	1.4±0.1	8.0±1.1	7.6±0.4	1.5±0.2

gas condensate is shown on Fig. 5. Along with identified peaks of tertiary amines there are some unidentified signals.

Results of quantitative analysis are presented in Table 1. Three technological points were studied before addition of new portion of the inhibitor (date 10.04.2013) and after addition (date 17.04.2013). Composition and ratio of amines are nearly same for all three point, with prevalence of N,N-dimethyl-dodecanamine. Addition of the inhibitor did not cause considerable changes of quantity of amines in the samples.

Summary

1. Major active components of corrosion inhibitor

CGW-85567 are C18:2 and C18:1 imidazolines and the corresponding imidazoline-amides.

2. HPLC/MS-technique allows determining concentration of the inhibitor in water solutions of MEG.
3. Low value of partition coefficient (0.010-0.014) of CGW-85567 in the system “water solution of MEG (concentration of MEG 62-85% v/v) - gas condensate” has allowed to pass on from the technology of continuous pumping of the inhibitor into protected pipelines to the periodic dosing technology.
4. Tentatively, N, N-dimethyl-dodecanamine, N, N-Dimethyl- tetradecanamine and N, N-Dimethyl-decanamine are degradation products of the CGW-85567 corrosion inhibitor.

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