

Hydrocarbon-Soluble Alkylaniline/Formaldehyde Oligomers as Corrosion Inhibitors*

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SYNOPSIS

Hydrocarbon-soluble oligomers were prepared by the acid-catalyzed condensation of alkylanilines with formaldehyde. Highest molecular weight oligomers (MW ~ 6000) were obtained from alkylanilines prepared by the Friedel-Crafts alkylation of aniline with α -olefins. By NMR, it was shown that the oligomers contain structures corresponding to methylene-linked aromatic rings and methylene linked to both an aromatic ring and a nitrogen atom. The oligomers exhibit very good initial inhibition of metal corrosion in aqueous environment; and the inhibition is more persistent than that observed with monomeric analogs.

INTRODUCTION

The relationship between adsorption and the corrosion inhibitor effectiveness of organic compounds is well known. The corrosion of metals can be inhibited by nitrogen, sulfur, or oxygen compounds which adsorb strongly to the surface of the metal and interfere with either the cathodic or anodic reactions occurring at the adsorption site.¹ For applications such as acid pickling or petroleum production, straight-chain fatty amines are especially effective. These so-called "filming amines" adsorb through their amino group, and with their hydrocarbon chains extending into the aqueous phase form a protective monolayer film at the metal surface.² Since it is known that polymers adsorb stronger than their monomeric analogs of the same structure,³ it is expected that polymers will be better corrosion inhibitors than the corresponding monomers. Indeed, Annand and co-workers have shown that, because of multiple adsorption bonding, poly(4-vinylpyridine), poly(4-vinylpiperidine), and polyethyleneimine are better corrosion inhibitors than 4-ethylpyridine, 4-ethylpiperidine, or ethylenedi-

amine.^{4,5} Corrosion inhibiting chelating polythioesters⁶ and oligomeric aminoethylene imidazolines⁷ have also been described.

In the present work, we describe the synthesis of a new class of hydrocarbon soluble oligomers by the acid-catalyzed polycondensation of higher alkylanilines with formaldehyde. We became interested in these compounds as improved corrosion inhibitors because they contain long alkyl chains similar to those found in the "filming amines" and because the polyamine structure offers the potential for multiple adsorption bonding.

EXPERIMENTAL

Alkylaniline Synthesis

Alkylanilines of high *para*-isomer content were synthesized from the corresponding alkylbenzenes by conventional nitration/hydrogenation (N/H) procedure.⁸ The N/H route produces about 90% *para*-alkylaniline together with small amounts of the *ortho*-isomer. No *meta*-alkylaniline could be detected in the products by NMR. The alkyl side chains of these compounds are derived from branched dodecene (propylene tetramer) or straight-chain dodecene, respectively, and are a mixture of several isomers. Dodecylaniline (branched dodecyl) was obtained from the Monsanto Co.

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Table I Alkylaniline Properties

Alkylaniline ^a	BP (°C/mm)	Composition (%)							
		N (%)		¹ H-NMR			¹³ C-NMR		
		Theory	Found	Ortho	Para	N-Alkyl	Ortho	Para	N-Alkyl
<u>N/H Route</u>									
Hexylaniline (Br)	91-106/1.2-3.2	7.90	7.80	7	93	0			
Dodecylaniline (Br)	155-185/0.8	5.36	5.45	12	88	0	6	94	0
Dodecylaniline (St)	165-189/0.6-0.7	5.36	5.35	9	91	0			
Tridecylaniline (Br)	142-165/0.6-0.7	5.09	4.80	12	88	0	10	90	0
<u>A/A Route</u>									
Dodecylaniline (St)	181/0.7	5.36	5.41	58	10	31	63	7	30

^a Br = branched alkyl; St = straight-chain alkyl.

Alkylanilines of high ortho-isomer content were synthesized by the alkylation of aniline with straight-chain α -olefins using Friedel-Crafts catalysts.⁹ The aniline alkylation (A/A) route produces about 60% *ortho*-alkylaniline together with small amounts of the *para*-isomer and 20-30% of the *N*-alkyl compound. No *meta*-alkylaniline could be detected in the products by NMR. Analytical data are summarized in Table I.

Oligomer Synthesis

A typical oligomer preparation was carried out as follows: To a 2-L, three-necked flask equipped with

a mechanical stirrer, condenser, and thermometer was added 261 g (1.0 *M*) branched dodecylaniline, 200 g water, and 200 g (2.1 *M*) concentrated HCl. The mixture was stirred and 98 g (1.2 *M*) of 37% formaldehyde was added in portions over a period of 15 min. The reaction mixture which turned orange-brown was stirred for 2 h at room temperature, followed by 2 h at 90-100°C. The mixture was cooled to room temperature and was neutralized with 1828 g of 5% NaOH. The solid reaction product was separated from the liquids by decantation, washed with water, and dissolved in methylene chloride. Evaporation of the methylene chloride gave 298.7 g of brown-colored oligomer having a molecular weight

Table II Alkylaniline/Formaldehyde Oligomers

No.	Starting Alkylaniline ^a	Moles	Formaldehyde (37%) (mol)	Yield (g)	Molecular Weight ^b	N (%)	Solubility ^c	
							Xylene	<i>n</i> -Heptane
<u>N/H Route</u>								
1	Hexylaniline (Br)	0.05	0.08	10.4	940	6.3	S	I
2	Dodecylaniline (Br)	1.0	1.2	298.7	1140	4.7	S	S
3	Dodecylaniline (St)	0.54	0.86	145.2	700	4.5	S	S
4	Tridecylaniline (Br)	0.05	0.08	19.7	900	4.0	S	S
5	Tridecylaniline (Br)	0.05	0.06	16.3	820	4.3	S	S
6	Tridecylaniline (Br)	0.05	0.05	15.7	870	4.2	S	S
<u>A/A Route</u>								
7	Dodecylaniline (St)	0.1	0.1	30.5	6800	4.6	S	I
8	Dodecylaniline (St)	0.1	0.12	30.1	6600	4.5	S	I
9	Dodecylaniline (St)	0.2	0.32	60.0	2700	4.4	S	I

^a Br = branched alkyl; St = straight-chain alkyl.

^b Vapor pressure osmometry (45°C, toluene).

^c S = soluble; I = insoluble.

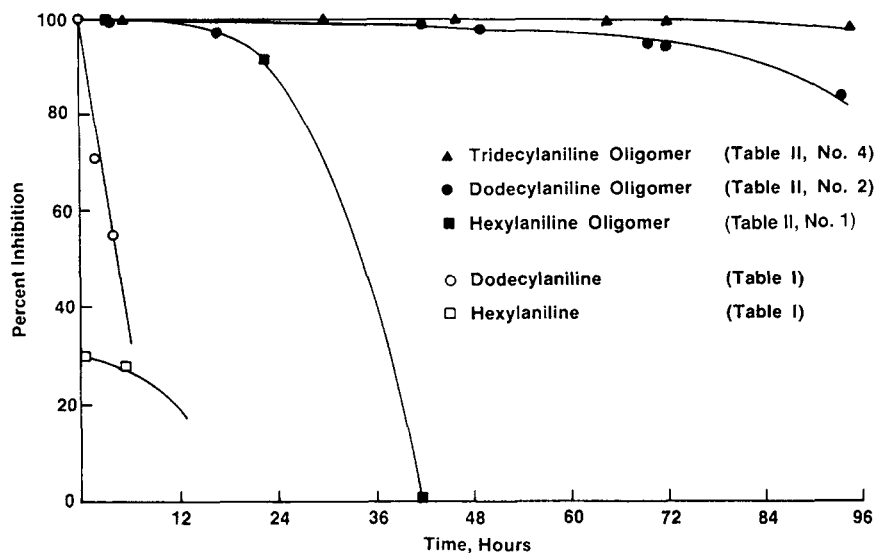


Figure 1 Inhibitor film persistence; 1 M HCl, 25°C, 10% dip treatment.

of 1140, as determined by vapor pressure osmometry. Nitrogen analysis of the oligomer showed 4.67% nitrogen.

The $^1\text{H-NMR}$ spectrum of the oligomer showed a broad, unresolved peak at 6.8–7.8 ppm (aromatic proton region). Completely absent from the oligomer spectrum were sharp peaks at 6.58, 6.60, 7.08, and 7.11 ppm, characteristic for the starting dodecylaniline. This indicated that the dodecylaniline had reacted completely to form the oligomer.

Infrared analysis of the oligomer showed a strong absorption in the 3395 and 3481 cm^{-1} region, indicative of $-\text{NH}_2$ groups. Other oligomers and cool-

omers were prepared by essentially the same procedure and are summarized in Table II.

Corrosion Inhibitor Evaluation

Corrosion rates (CR) were determined by the standard linear polarization method.¹⁰ Inhibitor evaluation, using a dip method, was carried out by immersing mild steel coupons in a 10 wt % solution of the inhibitor in kerosene for 30 min. The coupons were then rinsed with pure kerosene and reimmersed in the corrosion solution. An initial percent inhibition was recorded once a stable corrosion rate was

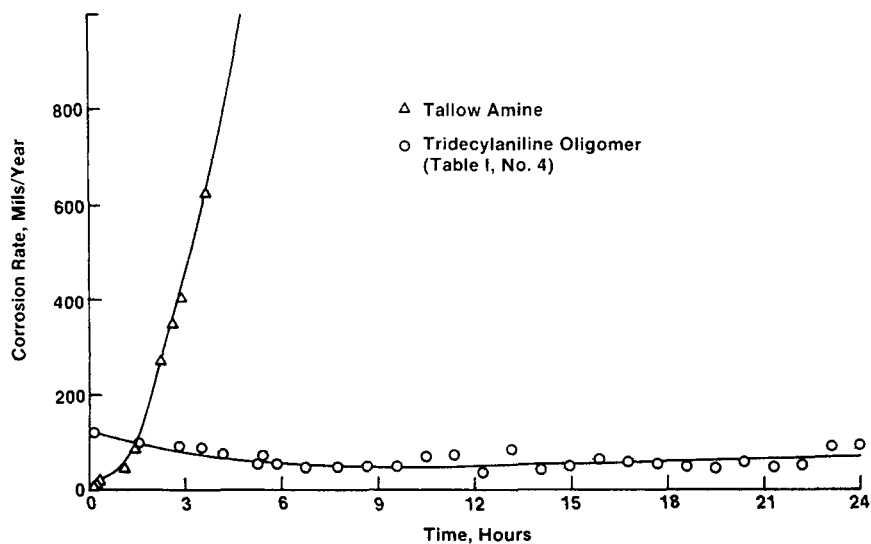


Figure 2 Inhibitor film persistence; 1 M HCl, 90°C, 2500 ppm dispersible formulation.

reached, typically within 30 min. For simulated oil field applications, the inhibitors were added as components of water-dispersible formulations to the corrosion solution.¹¹ The formulation used in Table V consisted of 25% alkyilaniline oligomer, 25% EM-POL 1024 dimer/trimer acid, 4% IGEPAL CO-630 nonionic surfactant, 42% kerosene, and 4% isopropanol. The formulation used in Figure 2 consisted of 20% amine, 35% decanol, 35% dodecanol, and 10% nonionic surfactant.

The percent inhibition was calculated as follows:

$$\% \text{ inhibition} = (\text{uninhibited CR} - \text{inhibited CR}) \times 100 / \text{uninhibited CR}$$

The film persistence of the corrosion inhibitors was determined by monitoring the inhibited CR as a function of time.

NMR Spectra

Proton and carbon-13 NMR spectra were recorded on a Varian VXR-300 instrument using conditions suitable for quantitative analysis.¹² The composition of the alkyl anilines (Table I) was determined from the resonance positions of the carbon-13 sites in *o*-, *p*-, and *N*-alkyl anilines.¹³ In mixtures of these compounds, the proton resonances could be assigned by their relative intensities once the composition of the mixture was roughly determined by the carbon-13 spectrum. The details of these experiments will be discussed elsewhere.¹⁴ The relative ratios of oligomer structures, discussed in Table III, were calculated from the carbon-13 spectra. The aliphatic-to-aromatic proton ratio of the oligomers was determined from the proton spectra and was used to confirm the structural assignments.

RESULTS AND DISCUSSION

Alkyilaniline/Formaldehyde Oligomer Synthesis

Previous work on the acid-catalyzed polycondensation of aniline with aqueous formaldehyde gave insoluble, crosslinked, nevertheless thermoplastic resins.^{15,16} *Meta*-toluidine also produces insoluble polymer but the condensates of *ortho*- and *para*-toluidine are soluble materials.¹⁷ One of the reaction products obtained from *para*-toluidine and formaldehyde is a chinazolidine (Troeger's base).¹⁸ The polycondensation of aniline is believed to proceed through the methylene-bis-aniline intermediate which rearranges into polymeric anhydro-*p*-ami-

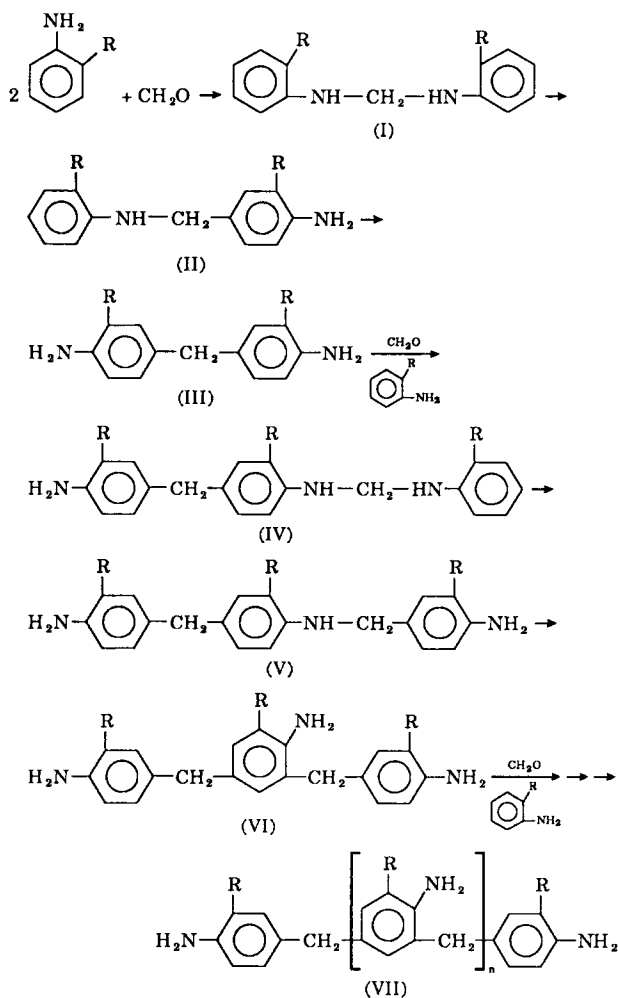
Table III Structure of Alkyilaniline/Formaldehyde Oligomers

Oligomer	MW	N (%)				¹³ C-NMR				¹ H-NMR, Aliphatic-H/ Aromatic-H			
		Theory ^c		Found		Aliphatic-C/ Aromatic-C		Structure IV (%)		Structure V (%)		Structure VII (%)	
		Found	Theory ^c	Found	Theory ^c	Found	Theory ^c	Found	Theory ^c	Found	Theory ^c	Oligomer	Alkyilaniline
Tridecyilaniline Oligomer (Br) ^a	900	4.0	4.9	2.5	2.3	10	65	25	9.1	6.8			
Dodecyilaniline Oligomer (St) ^b	6600	4.5	5.1	2.3	2.2	0	30	70	8.5	5.9			

^a Table II, No. 4.

^b Table II, No. 8.

^c Repeating unit of VII.



Scheme 1

nobenzylalcohol and, ultimately, into a polymer with methylene-linked aromatic rings.¹⁹

The polycondensation of higher alkylnilines with formaldehyde has not been reported before. We have found that with HCl catalyst, higher alkylnilines, and aqueous formaldehyde yield noncrosslinked oligomers. Experimental results are summarized in Table II. Highest molecular weight products were obtained from alkylnilines prepared by the A/A route. This result can be explained with the high *ortho*-isomer content of the starting alkylnilines which have at least one sterically unhindered ring site (*para*-amino) available for reaction with formaldehyde. The presence of *N*-alkylanilines, which are trifunctional, probably also promotes the formation of slightly crosslinked, but still soluble, high molecular weight oligomers. On the other hand, the polycondensation of *N*/*H*-derived alkylnilines (predominantly *para*-isomer) will occur at two ster-

ically hindered *ortho*-amino positions, limiting the molecular weight of the oligomers.

All of the oligomers are soluble in xylene. The lower molecular weight compounds, except the hexyl derivative, are also soluble in *n*-heptane.

The synthesis was also extended to the preparation of alkylniline/aromatic compound/formaldehyde cooligomers. With aniline and phenol, small amounts of crosslinked insoluble cooligomer was formed. The cooligomers with ethoxylated alkylnilphenol are completely soluble and are of particular interest because they form stable dispersions with hydrocarbons and water.

Oligomer Structure

A probable reaction sequence for the condensation of an *ortho*-alkylaniline with formaldehyde is shown in Scheme 1. Oligomer analytical data are summarized in Table III.

The formation of these compounds can be explained via methylene-bis-aniline and polymeric anhydro-*para*-aminobenzylalcohol type intermediates, similar to those postulated for aniline/formaldehyde resins.¹⁹

The ¹³C-NMR spectrum of the oligomers is consistent with the presence of VII (methylene linked to two aromatic rings; peaks near 140 ppm), V (methylene linked to an aromatic ring and a nitrogen; peaks near 140 and 148–154 ppm), and IV (methylene linked to two nitrogens; peaks near 160

Table IV Corrosion Results—DIP Treatment

Inhibitor	Initial Percent Inhibition	
	3% NaCl/CO ₂ , 25°C	1M HCl/N ₂ , 25°C
Hexylaniline (Br) ^a	22	53
Dodecylaniline (Br) ^a	0	99
Tridecylaniline (Br) ^a	20	99
Hexylaniline Oligomer ^b	99	99
Dodecylaniline Oligomer ^c	89	99
Tridecylaniline Oligomer ^d	97	99

^a Table I.

^b Table II (No. 1).

^c Table II (No. 2).

^d Table II (No. 4).

Table V Corrosion Results^a—Dispersible Formulation

Inhibitor	MW	Percent Inhibition		
		25 ppm Formulation	50 ppm Formulation	100 ppm Formulation
Tridecylaniline Oligomer (Br) ^b	900	64	95	99
Dodecylaniline Oligomer (St) ^c	700	71	98	99
Dodecylaniline Oligomer (St) ^d	2700	89	96	99

^a CO₂, 25°C.^b Table II, No. 4.^c Table II, No. 3.^d Table II, No. 9.

ppm). In the higher molecular weight A/A-derived alkyylaniline oligomers, VII predominates indicating a high degree of rearrangement of the methylene-bis-aniline intermediate during oligomerization. In the lower molecular weight N/H-derived alkyylaniline oligomers, the rearrangement of the methylene-bis-aniline intermediate is less complete and the most abundant structural element is V. Although the ¹³C-NMR gives an aliphatic-to-aromatic carbon ratio which is slightly higher and a nitrogen percentage which is lower than that required by VII, this may be caused by chinazolidine formation¹⁸ and, consequently, higher formaldehyde incorporation.

The ¹H-NMR spectrum of the oligomers shows a greater aliphatic-to-aromatic hydrogen ratio than that present in the starting alkyylanilines. This is consistent with the disappearance of aromatic hydrogens during oligomerization and furnishes proof for Structures V and VII.

The IR spectrum of the oligomers shows a broad, unresolved absorption at 3330–3500 cm⁻¹ (maximum at 3360 cm⁻¹) indicative of primary and secondary amino groups.

Corrosion Inhibitor Evaluation

The corrosion inhibitor performance of monomeric and oligomeric alkyylanilines, evaluated using the dip method, is shown in Table IV and Figure 1. The improved performance of the oligomeric materials can be ascribed to their multiple adsorption sites for bonding with the metal sample. This feature provides both for a thermodynamically favored bonding to the metal surface, due to the entropy effects from the greater number of solvent molecules displaced per polymer molecule, and a kinetically slower desorption step due to the multiple bonding sites.

Corrosion inhibitor evaluation using the disper-

sible formulation procedure is shown in Table V and Figure 2. It appears that the A/A route derived straight-chain dodecylaniline oligomer is somewhat better than that derived by the N/H route. These performance differences are probably caused by the higher molecular weight of the former oligomer. The tridecylaniline oligomer provides good protection for mild steel coupons, even under very severe corrosion conditions (1 M HCl, 90°C). Under comparable conditions, commercial tallow amine (a mixture of C-16 and C-18 fatty amines) loses its effectiveness in less than 2 h. Reports in the literature indicate that aromatic amines are poorer inhibitors than aliphatic amines.²⁰ This is probably caused by the weaker base strength of the aromatic amines, which results in weaker adsorption to iron surfaces. Therefore, the data of Figure 2 provide evidence that, in alkyylaniline/formaldehyde oligomers, the weaker base strength is amply compensated for by the availability of multiple adsorption sites for bonding.

It can be concluded that although most of the aniline derivatives show some corrosion inhibitor activity under strong acid or CO₂ corrosion conditions, the higher molecular weight oligomeric materials are clearly superior to their monomeric analogs.

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