Adhesive Properties of Novel Polyurethane Coatings Modified with Phenolic Compounds

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Novel polyurethane coatings for tar-free heavy-duty anti-corrosive coatings were developed by using phenolic compounds as a modifier. In order to establish basic concept for a design of a high performance polyurethane coatings, the relationship between adhesion strength and modification with phenolic compounds were studied. In this study, various phenols and naphthols were used as modifier, and the adhesion strength on sand-blasted steel sheet was evaluated. For example, 2-naphthol as a modifier for the thermosetting coating was reacted with isocyanate-oligomer and prepared the partially capped isocyanate with 16-25% of the total isocyanate group (see Fig.1). The partially capped isocyanates were reacted with polyols (see Fig.2) and modified polyurethane were formed. The recipes of modified polyurethane coating were shown on Table 1 and Table 2.

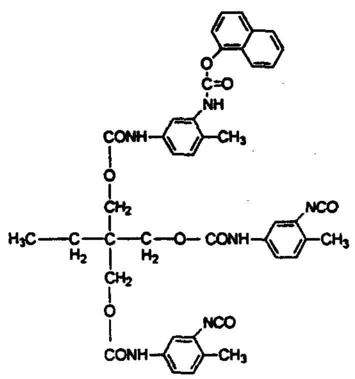

Fig. 1 Typical structure of partially capped isocyanate with 2-naphthol.

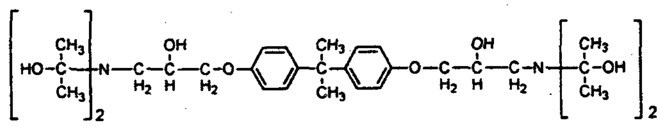

Fig. 2 Molecular structure of polyol.

Table 1 Recipe of modified polyurethane coating with different reduced ratio of NCO group

	A-0	A-1	A-2
<Polyol>			
EPO-0 50wt% toluene-MIBK-MEK	15.0 g	15.0 g	20.0-23.0 g
<Polyisocyanate>			
TDI-TMP 75wt% butyl acetate solution	24.0 g	24.0 g	22.1-28.8 g
<Phenols>			
2-Np	0 g	1.1-4.3 g	0 g
<Solvent>			
Toluene : MIBK : MEK = 5 : 3 : 2	46.0 g	48.5 g	48.4-56.5 g
Reduced ratio of NCO group*	0%	10-40%	10-40%

*on the basis of A-0

Table 2 Recipe of modified polyurethane coatings with different phenols

	B-1-1	B-1-2	B-1-3	B-2-1	B-2-2	B-3-1	B-3-2
<Polyol>							
EPO-0 50wt% toluene-MIBK-MEK solution	15.0 g	15.0 g	15.0 g	10.0 g	10.0 g	10.0 g	10.0 g
<Polyisocyanate>							
TDI-TMP 75wt% butyl acetate solution	36.0 g	36.0 g	36.0 g	24.0 g	24.0 g	24.0 g	24.0 g
<Phenol*>							
Ph	3.5 g						
2-Np		5.3 g					
4-ph-Ph			6.3 g				
p-tBu-Ph				3.7 g			
p-C9-Ph					5.5 g		
p-NO3-Ph						3.4 g	
1-NO3-2-Np							4.7 g
<Solvent>							
Toluene : MIBK : MEK = 5 : 3 : 2	72.2 g	76.5 g	78.8 g	51.3 g	55.4 g	50.7 g	53.6 g

*Amount of phenol is three times that at EPO-0 in mol.

The adhesion strength of the modified coating was 1.8 times higher than that of the non-modified coatings (see Fig.3).

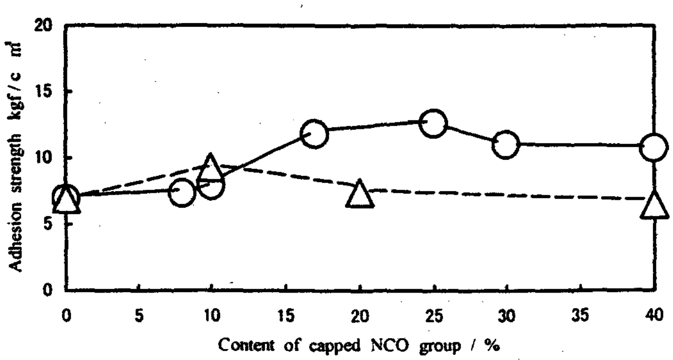

Fig. 3 Dependence of adhesive strength of the coatings on ratio of end-blocked NCO group (end-blocked coatings with 2-naphthol (○), and coatings with lower content of NCO group (△). The end-block ratio was calculated on the basis of the amount of NCO group in non-modified oligomers.

On the other hand, the adhesion strength of the coatings prepared from isocianate-oligomer with less amount of isocyanate group, showed only 1.3 times higher adhesive strength than that of the non-modified coatings. The results in Fig. 2 suggest the effect of the improved adhesive strength by modification of 2-naphthol was not only due to stress relaxation but also some additional effects. Furthermore, we studied the adhesive strength of the coatings with various phenols after the treatment with salt-water spray for 3000 h (see Fig.3 , Fig.4 and Fig.5).

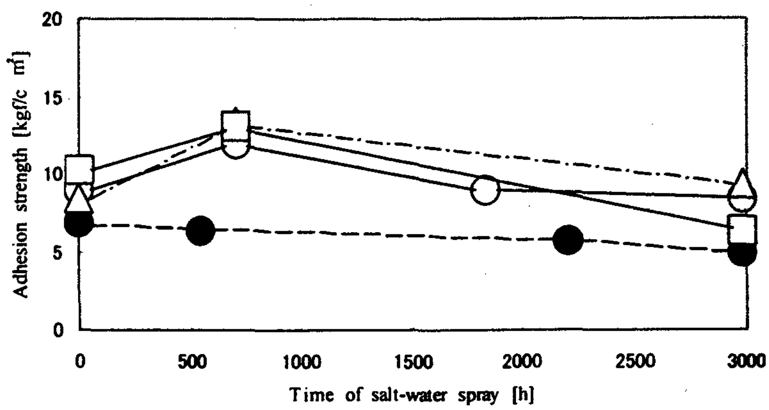

Fig.3 Relationship between the time of salt-water spray and the adhesion strength of the coating films prepared with different phenols on steel plate. (●);control, (○);Phenol, (△);2-naphthol, (□); 4-pnylphenol

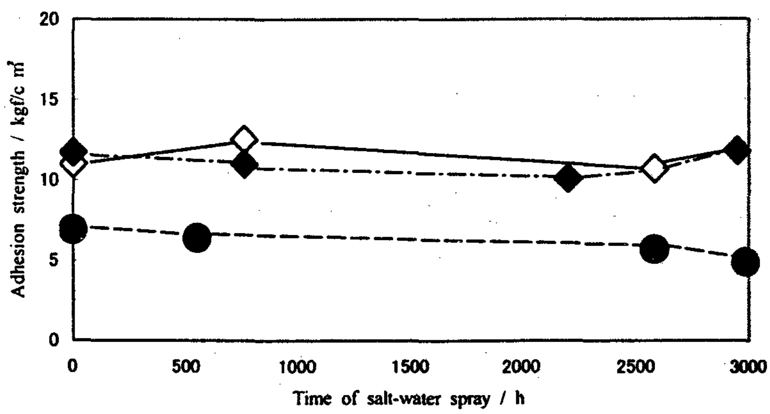

Fig.4 Relationship between the time of salt-water spray and the adhesion strength of the coating films prepared with different phenols on steel plate. (●);control, (◇);p-tert.-butyl-phenol, (◆);p-nonyl-phenol

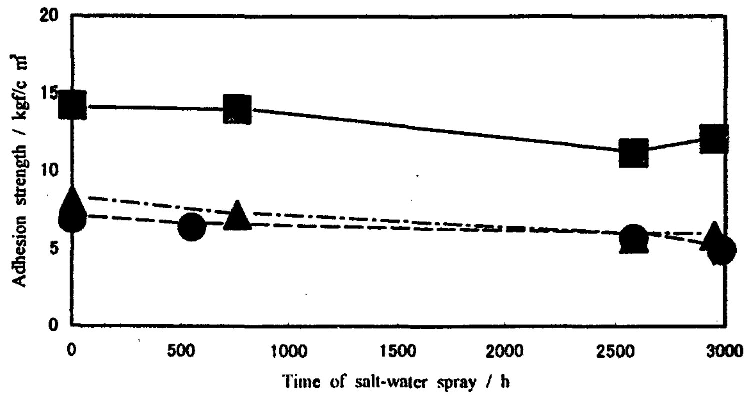

Fig.5 Relationship between the time of salt-water spray and the adhesion strength of the coating films prepared with different phenols on steel plate. (●);control, (○);phenol, (▲);p-nythoro-phenol, (□); 1-nythoro-2-naphthol

As the results, alkylphenol and nitrophenol as modifiers were more effective for increase of the adhesion strength. It was also found that the adhesive strength of modified coatings was depend on pK_a of the phenols, and better adhesion strength was given at $pK_a=7$ (see Fig.5).

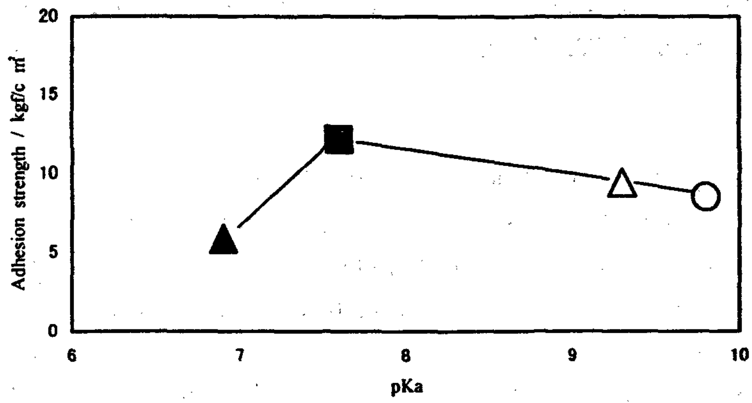

Fig.5 Relationship between the time of salt-water spray and the adhesion strength of the coating films prepared with different phenols on steel plate. (●);control, (○);phenol, (▲);p-nythoro-phenol, (□); 1-nythoro-2-naphthol

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