

# ***Inhibition of Discoloration in Acrylic Polymers***

## **INTRODUCTION**

It is well recognized that acrylic polymers and fibers tend to discolor on exposure to heat and alkali.<sup>1</sup> Factors affecting the discoloration of acrylic polymers and their preventive measures have been reviewed by Datye and Gupta.<sup>2</sup>

A large number of organic additives have been proposed in an attempt to overcome this problem. Some of the stabilizers used for prevention of discolouration are organic acids, organotin compounds, organophosphorous compounds, maleic anhydride and their derivatives, monoesters of glycerine, mercaptans, sequestering agents, and reducing agents as reported in the literature.<sup>3-24</sup> However, maleic anhydride does not inhibit discoloration in acrylic polymer solution.

We are therefore reporting the inhibition of discoloration in acrylic polymer solution using a number of organic additives as color stabilizers in this publication. An attempt has also been made to explain the action of potential stabilizer in solution.

## **EXPERIMENTAL**

Acrylic polymer [P(AN-VAC), 7.0% VAc] used for the present work is obtained by copolymerization of acrylonitrile and vinylacetate using  $K_2S_2O_8-SO_2-FeSO_4$  as the redox initiator system.<sup>25</sup>

Acrylic polymer solution is prepared by mixing polymer powder in dimethyl acetamide at low temperature (0–5°C) and heating the resulting slurry in a controlled water bath at 90°C till a clear solution is obtained. We have selected 20% polymer concentration for our present work. Organic additives have been added in the slurry in the concentration range of 0.0–0.20% based on polymer weight. These polymer solutions have been kept in glass bottles with plastic stopper and heated at 90°C for 5 h. A control sample without any additive has also been heated for same time interval. Optical density of these polymer solutions have been measured on DU-8 Beckman spectrophotometer at  $\lambda$  max of 425 nm. Laboratory grade chemicals and additives have been used for this study. Ethylene diamine tetra acetic acid (EDTA) was prepared from acidification of its disodium salt.

IR spectra of polymer samples (films) were recorded on a Perkin-Elmer 457 infrared spectrophotometer and a Unicam SP 1000 spectrophotometer.

## **RESULTS AND DISCUSSIONS**

Table I shows the effect of additives on optical density of acrylic polymer P(AN-VAC) solution in DMAC at  $\lambda$  max of 425 nm. Additives used for the present study were without further purification. Results of the Table I indicate that oxalic acid (OA), EDTA, maleic anhydride, phthaleic anhydride, *p*-toluene sulfonic acid, and lithium chloride used alone are not effective stabilizers as indicated by optical density values. Though these compounds are reported to inhibit discoloration as reported in the literature. Oxalic acid and *p*-toluene sulfonic acid inhibit discoloration to a little extent as indicated by OD values 0.3425 and 0.4195 compared to OD of control sample (0.4566). Maleic anhydride when used alone shows higher value of OD thus promoting colour forming reaction, contrary to observation made by Runge and Nelles.<sup>14</sup> When we used a mixture of additives, oxalic acid was selected as one of the essential component as it is being used (0.2% based on polymer weight) as a stabilizer by commercial acrylic fibre manufacturer. It was observed that mixture of oxalic acid and maleic anhydride are effective stabilizers for inhibition of discoloration as indicated by lowest OD (0.1544) in these polymer solutions. Most effective composition was 0.05% oxalic acid and 0.1% maleic anhydride.

Success of these stabilizers in inhibiting discoloration may be explained due to combining effect of individual stabilizers. Maleic anhydride inhibits the discoloration process by reaction with

TABLE I  
Optical Densities of Acrylic Polymer Solution at  $\lambda_{\text{max}}$  425 nm

Sample no.	Additive	Amount added (%)			OD at $\lambda_{\text{max}}$ 425 nm
		I	II	III	
1		—	—	—	0.4566
2	Oxalic acid (OA)	0.1	—	—	0.3425
3	EDTA	0.1	—	—	0.4401
4	Maleic anhydride (MAn)	0.1	—	—	0.4823
5	Phthalic anhydride (PhAn)	0.1	—	—	0.4944
6	<i>p</i> -Toluene sulphonic acid ( <i>p</i> -TSA)	0.1	—	—	0.4196
7	Lithium chloride	0.1	—	—	0.4677
8	OA + EDTA	0.05	0.05	—	0.2704
9	OA + MAn	0.05	0.05	—	0.2143
10	OA + PhAn	0.05	0.05	—	0.2311
11	OA + <i>p</i> -TSA	0.05	0.05	—	0.3042
12	OA + MAn	0.05	0.1	—	0.1544
13	OA + MAn	0.025	0.1	—	0.1752
14	OA + MAn	0.1	0.05	—	0.1905
15	OA + MAn	0.05	0.025	—	0.1947
16	OA + <i>p</i> -TSA	0.05	0.1	—	0.2690
17	OA + <i>p</i> -TSA	0.1	0.05	—	0.2357
18	OA + MAn + <i>p</i> -TSA	0.05	0.1	0.025	0.1463
19	OA + MAn + <i>p</i> -TSA	0.05	0.1	0.05	0.1499
20	OA + MAn + EDTA	0.05	0.1	0.025	0.1480
21	OA + MAn + EDTA	0.05	0.1	0.05	0.1465

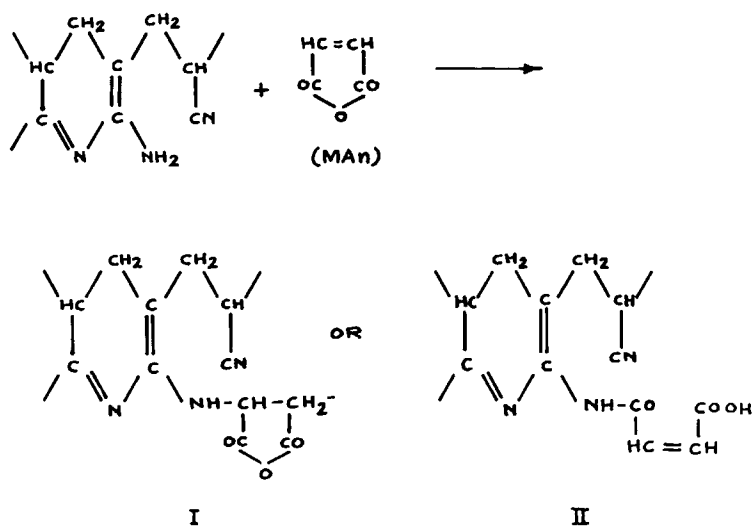


Fig. 1. Mechanism of inhibition of nitrile cyclization by maleic anhydride.

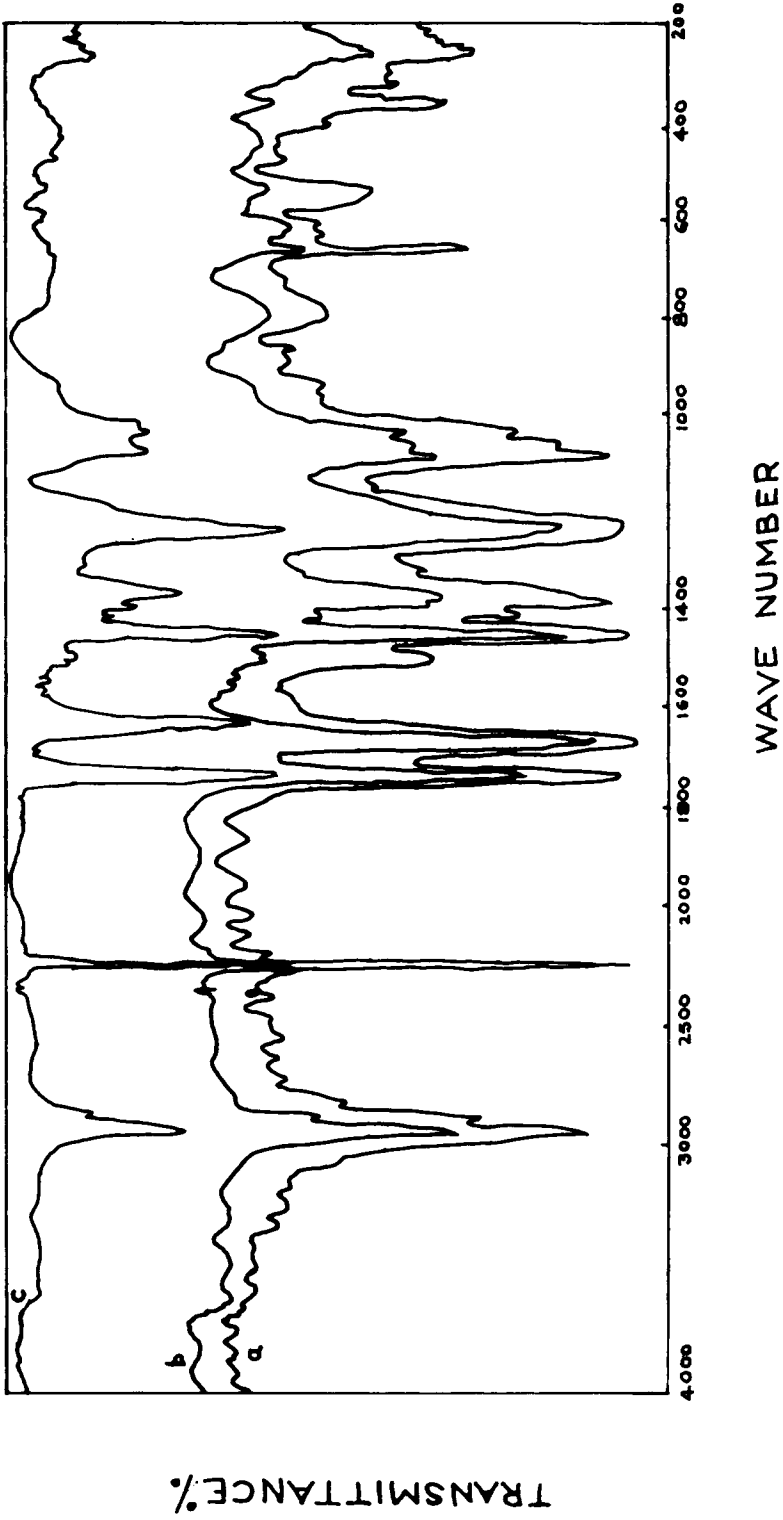


Fig. 2. Infrared spectra of (a) P(AN-VAc), (b) P(AN-VAc) in the presence of oxalic acid and maleic anhydride, and (c) recovered P(AN-VAc).

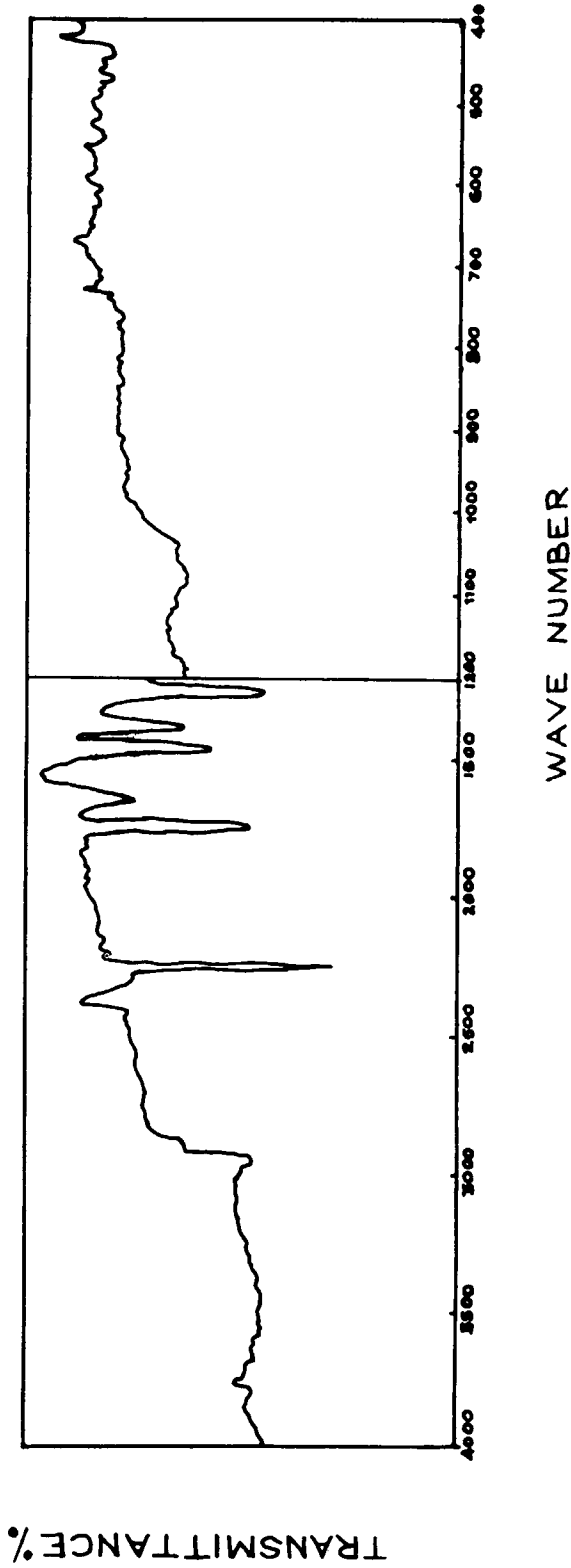


Fig. 3. Infrared spectra of P(AN-VAc) heated at 200°C for 20 min.

imine groups of cyclized PAN polymer residue cyclization of nitrile groups. Presence of oxalic acid may be enhancing the reaction of maleic anhydride with imine groups of oligomerized polyacrylonitrile. Oxalic acid and maleic anhydride when combined together does not allow the polymerization of nitrile groups to take place and effectively inhibit the discoloration process. Further oxalic acid protonate the polymeric imine groups and avoid the formation of cyclized structures as suggested in the patent literature.<sup>7,10,11</sup> Reaction of maleic anhydride with cyclized PAN is given in Figure 1.

Use of phthaleic anhydride in a similar amount does not produce an encouraging result. Phthaleic anhydride does not produce an encouraging result. Phthaleic anhydride does not inhibit discoloration, indicating that color stabilization reaction through route I (Fig. 1) is more predominant. Since phthaleic anhydride does not have unsaturated double bond, it fails to inhibit discoloration.

We have also selected three component stabilizers consisting of OA + MAn + EDTA and OA + MAn + *p*-TSA. Out of these two, oxalic acid and maleic anhydride along with EDTA is preferred for our further processing of polymer solution. The effect of these stabilizers in the inhibition of discoloration is greater compared to bicomponent stabilizers.

EDTA helps to remove discoloration caused by the presence of metal ions like  $\text{Fe}^{++}$  used as a promoter in polymerization. The function of *p*-toluene sulfonate is similar to that of any acid, since it is a Lewis acid. Hence the use of the oxalic acid-maleic anhydride-EDTA system is preferred over the system with *p*-toluene sulfonate. These three component stabilizers (OA-MAn-EDTA) are most effective stabilizers for inhibition of discoloration in acrylic polymer solution as compared to other systems.

The above results are further supported by IR studies as shown by IR of discolored acrylic polymer solution and of polymer solution with oxalic acid and maleic anhydride additives (Fig. 2). These IR spectra show a reduced amount of conjugated carbon-nitrogen bands at  $2060\text{ cm}^{-1}$  ( $2000\text{--}2160\text{ cm}^{-1}$ ) and at  $1490\text{--}1510\text{ cm}^{-1}$  compared to the peaks in IR spectra of the polymer sample without any additive. A further amount of the nitrile group is reduced as shown by peak height at  $530\text{ cm}^{-1}$  in IR of polymer with additive, though the principle peak due to the nitrile group ( $\text{--C=N}$ ) at  $2250\text{ cm}^{-1}$  is of the same height in both the samples. However, the effect of discoloration on the peak height at  $2250\text{ cm}^{-1}$  is clearly understood if dope is heated for longer time (2-3 days) or dope is collected from an acrylic plant which was recovered from various operations for reuse. IR spectra of recovered dope give reduced peak heights due to  $\text{--C=N}$  groups. IR spectra of heated polymer samples ( $200^\circ\text{C}$  for 20 min) also give a reduced peak due to these nitrile groups at  $2250\text{ cm}^{-1}$  (Fig. 3). Reduced peak heights due to nitrile groups ( $\text{--C=N}$  groups) observed in discolored polymer samples may be due to conversion of nitrile groups to conjugated carbon-nitrogen bonds ( $\text{=C=N--}$ ) as reported by Grassie and McGuchan.<sup>25</sup> IR spectra further suggest addition of stabilizers, minimizing the formation of conjugated carbon-nitrogen bonds of cyclized structures as evidence by reduced bands at  $2060\text{ cm}^{-1}$ .

Financial support from University Grants Commission (U. G. C.), New Delhi to one of us (R. C. S.) is gratefully acknowledged. We are thankful to Principal, Govt. College KOTA for providing facilities for the work.

## References

1. R. C. Houtz, *Text. Res. J.*, **20**, 786 (1950).
2. K. V. Datye and D. C. Gupta, *Synth. Fibres XIII*(1), 6 (1984).
3. A. Decorte, *Text. Chim.*, **27**(4), 4 (1971); *Text. Abstr.*, 6177 (1971).
4. U. Mayer and A. Wiirz, *Acrylic Manual* (BASF), p. 58.
5. H. F. Mark, H. J. Mcketta, Jr., and D. F. Othmer, *Encyclopedia Chemical Technology*, Wiley, Interscience, New York, 1967, Vol. 6, p. 22.
6. B. M. Pettyjohn and S. C. Camden, U. S. Pat. 3,383,350 (1968).
7. N. Gransie and I. C. McNeill, *J. Polym. Sci.*, **39**, 211 (1959).
8. N. Gransie and J. N. Hay, *Soc. Chem. Ind. London, Monogr.*, **13**, 184 (1961).
9. Japan Exlan Co., Br. Pat. 1243292 (1971); W. Test. Abstr., 5791 (1971).
10. D. R. Thomson, U. S. Pat. 3755230 (1973).
11. Monsanto Co., Br. Pat. 1423713 (1976).
12. Monsanto Co., Br. Pat. 1423852 (1976).

13. E. M. Grant, Br. Pat. 1,138,945 (1969); *W. Text. Abstr.*, 645 (1969).
14. J. Runge and W. Nelles, *Faserforsch. Text. Tech.*, **21**, 105 (1970); *Chem. Abstr.*, **72**, 22303n (1970).
15. Z. Adamski, *Preze Wlok*, **25**, 159 (1971); *W. Text. Abstr.*, 5371 (1971).
16. Z. Adamski, *Zes. Nauk. Polit. Lodz. Wlok.*, **25**, 5 (1973); *W. Text. Abstr.*, 1562 (1974).
17. R. Zoller, W. Fester, F. Jakoh, and A. Dahmen, U. S. Pat. 3,778,416 (1973); *W. Test. Abstr.*, 788 (1974).
18. J. J. Hirshteld and B. T. Reaban, U. S. Pat. 3,462,238 (1969); *W. Test. Abstr.*, 607491964 (1969).
19. K. W. Krebs, H. Engelhard, and G. Nischk, Br. Pat. 1360669 (1974).
20. D. E. Steutz and K. H. Gump, Br. Pat. 1,264,026 (1972); *W. Test. Abstr.*, 2100 (1972).
21. K. Kozuka, S. Kurioka, T. Yasumoto, S. Kobayashi, A. Kubota, and N. Ootoshi, U. S. Pat. 4,002,809, (1977); *W. Test. Abstr.*, 1482 (1977).
22. Japan Exlan Co., Br. Pat. 1,256,455 (1972); *W. Text. Abstr.*, 345 (1972).
23. D. W. Cheap Jr. and J. J. Hirshfed, U. S. Pat. 3354113 (1967).
24. D. C. Gupta, *J. Appl. Polym. Sci.*, **30**, 4193 (1985).
25. N. Graasie and R. McGuchan, *Eur. Polym. J.*, **8**, 865 (1972).

D. C. GUPTA\*  
R. C. SHARMA

Sir Padampat Research Center  
J. K. Synthetics Ltd.  
Kota Pin, 324003 Rajasthan,  
India  
Dept. of Chemistry  
Govt. College  
Kota Pin, 324006 Rajasthan,  
India

\*Present address: Applied Polymer Division, E.R.D.L. Pune 411 021, India

Received September 21, 1989

Accepted September 25, 1989