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An Investigation of Curing Melamine/Alkyd resin mixtures with Differential Scanning Calorimetry

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The aim of this work consisted in investigating the possibility to determine the optimum curing temperature for alkyd (AR)/melamine(MR) resin mixtures used as binders in the coating industry from DSC measurements on pure components and various AR/MR mixtures.

In industry high quality performace coatings, e.g. in automobile production, are obtained by combining AR and MR. The curing of the two components in the paint formulation is effected with acid catalists at room temperatures or by baking within 80-160^{o} (1). The recommended AR/MR ratio is 70·30 % wt., but in systems cured at lower temp. or with acid catalysts the content of MR may reach 50 %.

The reactions and physical phenomena taking place during curing in the AR/MR systems are not yet fully understood. In the curing of pure AR with high unsaturation and substantial acid (AN) and hydroxyl numbers (OHN), considered from the standpoint of thermal analysis, the following exothermic (EX) and andothermic (EN) general reactions are to be taken account of (2-5):

1) Polymerisation of unsaturated C=C bonds	EX
2) Oxydative polymerisation with atomos. oxygen	EX
3) Esterification of -OH and -COOH, water eliminated	EN
4) Transesterifications of -OR and -COOR, ROH elim.	EN
5) Evaporation of elimination products of 3) and 4)	EN
6) Evaporation of solvents and thinners	EN

In pure MR the following reactions predominate:

7) Methylene bridges formation, water eliminated	EN
8) Methyleneether bridges formation, water eliminated	EN
9) Evaporation of elimination products from 7) and 8)	EN
10) Evaporation of solvents and thinners	EN

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In combined AR/MR systems intra-crosslinking most probably occurs via bridges formed by reacting AR-OH and AR-COOH with MR $-NH.CH_2OH$ and $-NH.CH_2.OR$ groups, forming thus mixed ether and ester bridges (summative intra-crossliking reactions designated 11). The rates of reactions 1) and 2) depend on the extent and type of unsaturation; regarding the temp.influence, reactions 1,2,7,8 and 11, catalysed or autocatalysed will start at lower temperatures than 3,4, favouring thus intra-crosslinking. For TA reactions 6,10 can be minimized by predrying the samples at low temp., and 5,9, by performing experiments in Al-pans for volatile samples.

Materials: AR represented commercial phalic anhydride and dehydrated castor oil (33 and 45%) based products, with AN 20-25 and ONH from 50 to 100 as 60% solutions in high boling aromatics. MR were highy alkylated commercial products as 55% solutions in 9:1 isobutanol/xylene. In developing the experimental procedure sealed Al-pans for volatile samples and resin solution mixtures were soon discarded because of leakages of volatiles when raising the temp. Therefore the resins or resin mixtures were dried for 2 h. at 50^O i.vac. and then transfered to open pans, thus eliminating reactions 5,9. The samples investigated were pure AR (Fig.1), MR (Fig. 2) and AR/MR 85/15 (Fig.3), 80/20, 75/25 and 70/30 mixtures, the temp. interval of interest $323\text{-}523^OK$. On the basis of dinamic mesurements, temp. of 413, 423, 453^OK and others were selected for isothermal experiments.

Discussion: The thermogram for AR (33% oil) is strongly exothermic both in nitrogen and air in the range of 363-463 with a minimum at 433^OK indicating predominantly reaction 1). At still higher temp. degradation begins. The pure MR (Fig. 2) is strongly endothermic in the range of $380\text{-}480^OK$, a small shoulder and then a maximum at near 445^OC, resulting from various types of reactions 7,8 and 9.

Fig. 3 is one of the many tupical thermograms obtained for AR/MR mixtures. Two typical regions can be distinguished: a) an exothermal beginning of the reaction at 370^OK, present also in the pure AR, with an exothermal peak at near 420^OK and b) an endothermal overall reaction region, preseded by a shoulder, with a peak near 465^OK, and a return to the baseline near 490^OK. From this type of thermogram it is evident that polymerization crosslinking of the AR portion is the first reaction, not involving any of the groups undergoing condensation, and that inter-condensation begins at a later stage when the unsaturated groups have already reacted.

Similar types of theromograms were obtained for other AR/MR ratios. With decreasing AR the exothermal surface decreased and the endothermal increased. The extent of unsaturation of the AR, expressed either in terms of iodine number or castor oil content also influenced the exo/endo surface of the thermograms.

Regarding optimization of the curing temperature for AR/MR mixtures of this type, in our further work it was attempted to shift the endothermal maximum to lower temperatures, by incorporation of condensation catalysts and/or AR with still higher AN, expecting thus both polymerisation and polycondensation to take place at a common lower temperature, in order to save energy during baking and also in order to obtain a more uniform crosslinked structure of the two components.

Similar investigations are not numerous in the literature. The work of Gauler (6) which represented a guideline for the experimental part, used AR based on saturated fatty acids and hexamethoxymethyl melamine, which exhibits exothermicity in the first reaction step. Our investigation is being continued.

The thermograms were taken on a perkind-Elmer DSC-2 instrument with a maximum sensitivity of 0,1 mcal s^{-1} for a full scale deflection.

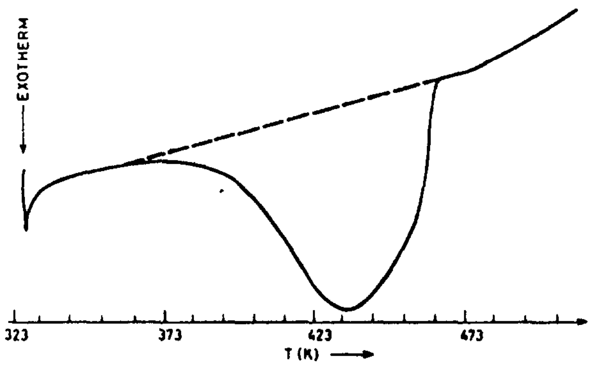

FIG 1

Fig. 1.

Thermogram for pure Alkyd resin with 33% wt of dehydrated castor oil, heating rate 10 K/min, range 1 mcal/s, weight 18,5 mg

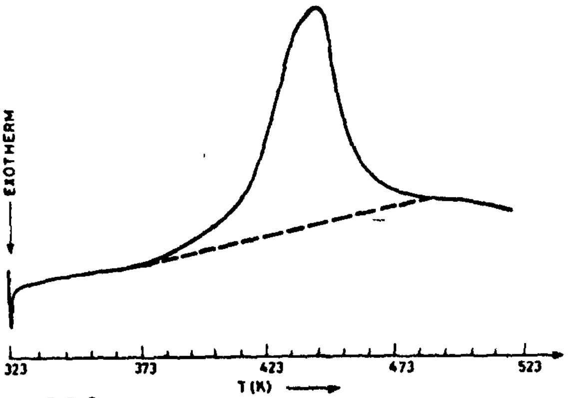

FIG 2,

Fig. 2.

DSC Thermogram for pure Melamine resin, highly alkylated, heating rate 10°K/min, range 1 mcal/s, weight 18,2 mg

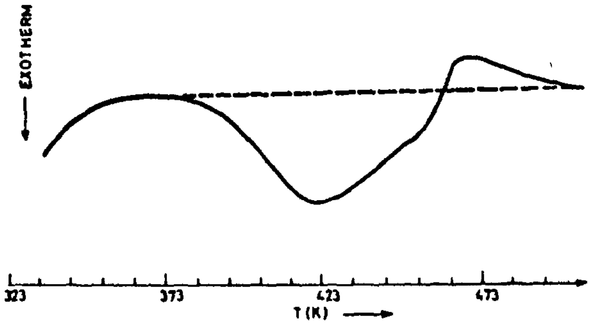

FIG 3

Fig.3.

DSC Thermogram for a 85/15 alkyd/melamine mixture, heating rate 10°K/min, range 1 mcal/s, weight 30,1 mg

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