

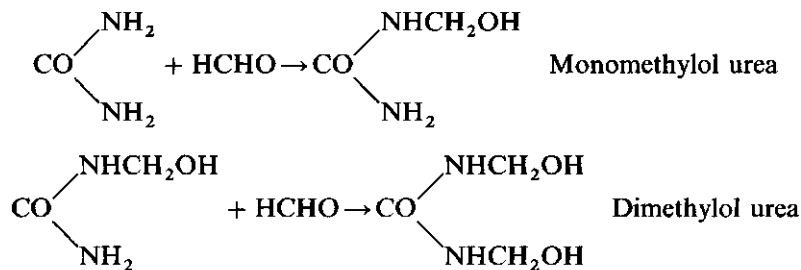
5 Easy care

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5.1 Introduction

Amino resin finishing commenced in the early 1920s when Tootal Broadhurst Lee took patents out on the manufacture of simple urea-formaldehyde resins for the production of crease-resistant fabrics (Foulds *et al.*, 1926). Those original patents also included phenol formaldehyde as well as urea; the phenol formaldehyde could be discounted due to its colour. But Tootal Broadhurst Lee commercialised on their patent and built up a world wide licensing organisation where companies licensed the process, and when they produced the required standards of crease resistance and tensile strength were granted the Tebilized (Registered Trade Mark) label.

The general formulation for production of the resin was as follows. The product itself would have a limited shelf life dependent on local conditions, pH conditions and temperature.



The process required an acid catalyst together with a drying and curing schedule which is still practised in modern resin finishing. The manufacture of own-made resin was still prevalent in the UK until 1993, when the last two companies producing their own-made precondensate ceased production and went over to a manufactured precondensate.

After urea a full range of products was developed, each one containing formaldehyde, such as the following (Figure 5.1).

1. Urea-formaldehyde
2. Highly condensed urea-formaldehyde
3. Methylated urea-formaldehyde
4. Melamine-formaldehyde
5. Methylated melamine-formaldehyde

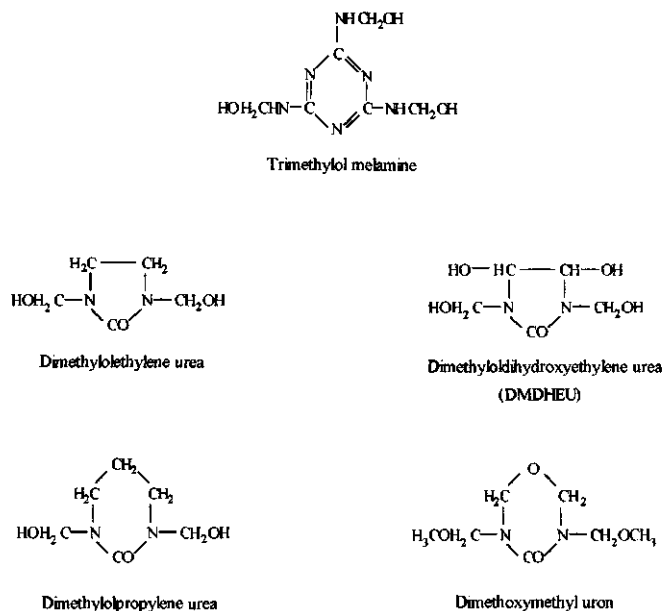


Figure 5.1 Examples of major resins used in the industry and their chemical structures.

6. Ethylene urea–formaldehyde
7. Heterocyclic crosslinking agents based on melamine–formaldehyde
8. Glycol based reactants and derivatives thereof.

Each of these resins has its own particular part in the evolution of easy care finishes to produce present day standards.

The properties required by an easy care finish are:

1. Dry and wet crease resistance
2. Good dimensional stability
3. Little loss in physical properties (i.e. tensile and abrasion)
4. Compatibility with other finishing agents (e.g. water-repellent, softeners, optical brightening agent)
5. Minimum effect on handle
6. Little effect on dye or print shade or the light-fastness of the dye
7. Little effect on rub fastness of dye or print
8. No effect on the whiteness of the fabric
9. As low as possible formaldehyde release
10. Good environmental condition both in the application of the resin and the final making up of the fabric when finished
11. Ease of application and low cost add-on factor in both chemical and application cost.

5.2 Urea–formaldehyde resins

These products were initially produced in-house by various organisations and licencees of the holders of original patents (mainly Tootals and Courtaulds). However, due to the high free formaldehyde content of the resin, which ranged around 5% (present products have less than 0.5% on comparative solid levels), washing-off of the fabric was required after finishing. During the period of development of urea–formaldehyde resins, the advent of viscose rayon came about, and without resin finishing, this type of fabric would never have gained the popularity it did in the years prior and subsequent to the Second World War.

5.3 Methylated urea–formaldehyde resins

Coming onto the market in the early 1950s, these products (such as Kaurit W, BASF, BT 322, BIP) produced product stability well in advance of six months, and therefore opened up the field of resin finishing to companies who had previously been unable to carry out chemical finishing due to lack of knowledge of resin manufacture. Also at the same time a fashion trend for nylon petticoat finishing came about, and it was found that methylated urea–formaldehyde resins were able to produce durable stiff finishes on nylon. By the addition of thiourea, flame resistance of the nylon fabric was also obtained.

Comparison of the finishing of viscose rayon or cotton with that of nylon with a methylated urea–formaldehyde resin may be illustrated as follows. With the cotton fibre, the resin enters into the fibre and, when catalysed, produces a polymeric network structure in the fibre that prevents the fibre from creasing and shrinking on washing. With nylon, the resin forms a complete bond and produces a sheath-like coating to the fabric which is durable and stiff (Figure 5.2).

Methylated urea–formaldehyde resins also had the advantage over home-made precondensates that, when applied to nylon, they did not produce 'chalking or writing on the fabric' as did simple urea–formaldehyde resins.

Other advantages, methylated urea–formaldehyde resins have greater durability to washing and also produce better shrink-stability of the treated fabric.

The molecular sizes of the methylated urea–formaldehyde resins are very small, which enables them to enter the fibre to produce the crease resistance and stability, the size of the molecule remaining stable. However, in the case of straight urea–formaldehyde resins, the molecular size is not stable and is increasing all the time. Subsequently the size of the molecule becomes so large that it falls out and the resin becomes unusable. This is not the case with the methylated urea resins until they are catalysed, when the stability of the bath may be in the order of 24–48 h.

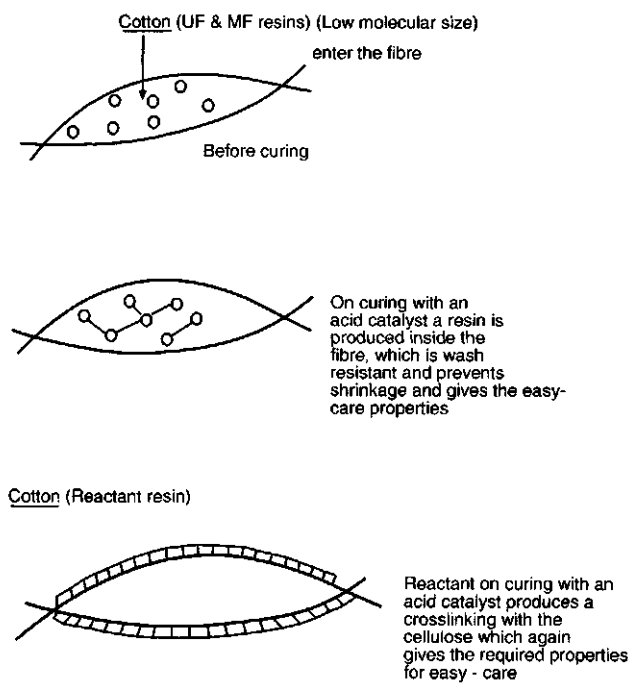


Figure 5.2 Comparison of reaction of resin former and a reactant with cellulose fibre.

Using the above knowledge, chemical manufacturers have been able to produce high molecular size urea-formaldehyde resins which may be used to stiffen or bond fibres together. These resins simply stay on the surface of the fibre and produce a stiffened effect rather than a crease-resistant effect. These resins are very rarely used on their own for finishing fabrics but are generally incorporated with crease-resistant resin to produce the 'handle' required. Typical formulations for a normal crease-resistant finish on viscose rayon are as follows.

| | |
|--------------------------------------|-------|
| Urea-formaldehyde resin (40% solids) | 300 g |
| Cationic softener | 20 g |
| Monoammonium dihydrogen phosphate | 3 g |
| Water to 1 litre | |
| Mangle expression | 75% |

To increase the 'spring' and 'handle' the formulation could be

| | |
|---|-------|
| Urea-formaldehyde resin (40% solids) | 260 g |
| Highly condensed urea-formaldehyde (50% solids) | 40 g |
| Cationic softener | 20 g |

| | |
|-----------------------------------|-----|
| Monoammonium dihydrogen phosphate | 3 g |
| Water to 1 litre | |
| Mangle expression | 75% |

5.4 Melamine resins

These resins were the next resin group to appear, and initially two major products were predominant, dimethylol melamine and trimethylol melamine. Dimethylol melamine was unstable and was mainly produced in a spray-dried (powder) form.

Trimethylol melamines were produced by A.C.C. in the USA (Aerotex M3), became widely used and are still used. The melamine resins were found to give a fuller handle on cotton and viscose than the urea-formaldehyde resins, but commercially they were more expensive. Four major niche markets were found for melamine resins and these still exist:

1. For durable mechanical finishes on cellulose
2. As a crosslinker for polymers such as acrylonitrile, acrylics, polyvinyl acetate, polyurethane, etc.
3. As a stiffener for polyester or nylon
4. As a handle builder in conjunction with other resins.

5.5 Mechanical finishing

Durable mechanical finishing came into vogue in the early 1950s and Joseph Bancroft produced the initial Everglaze (Registered Trade Mark) patent.

The principle of Everglaze is to produce a mechanical finish on the fabric that is wash-fast. This is carried out by impregnating the fabric with a solution of melamine resin plus catalyst, and drying the fabric to a moisture content of approximately 6–8% before carrying out the mechanical effect prior to a final curing. Typical formulations for this would be:

| | |
|---|------|
| Trimethylol melamine resin (80% cured solids) | 60 g |
| Magnesium chloride (40% solution) | 20 g |
| Silicone softener | 5 g |
| Water to 1 litre | |

Based on a 65% pick-up, this would give approximately 3.1% solids on the fabric. The required amount of melamine solids in the fabric should be in the region of 2.5–3.2%; higher solids may produce a better mechanical finish but would impair the physical properties of the fabric.

After impregnation, the operation of drying the fabric is a crucial part of the process. The moisture content must be fully controlled and a final moisture content of 6–8% should be obtained before mechanical finishing. Too much

moisture may produce an initial better mechanical finish but the durability will be poor, whilst too little moisture will give poor mechanical effects. It should also be remembered that if the fabric is overdried precure is brought about, and re-wetting cannot reverse the reaction. When precure takes place poor durability of the mechanical effect can take place. Types of mechanical finishes that are possible are as follows.

1. Glaze
2. Schriener
3. Sculptured or embossed
4. Permanent pleating

Once the mechanical effect has been produced on the fabric, the effect has to be made permanent by a curing process.

Figure 5.3 illustrates the type of equipment normally used for the process.

Glazing and schrienering of fabrics have kept in vogue of the last 25 years, but very little call has been made for permanent pleating, except for a brief period when Koratron (Registered Trade Mark) pleating became popular, this being overtaken by the advent of polyester-cotton, which itself was capable of producing its own permanent crease effects.

The use of melamine and urea resins for finishing produced a number of unwanted elements, the major one being 'fishy odour' or amine smell, and the next section deals in depth with this.

5.6 The problem of fishy odour in resin-treated fabrics

One of the problems which sometimes arises out of the application of crease-resist finishes and related processes is the spasmodic and frequently

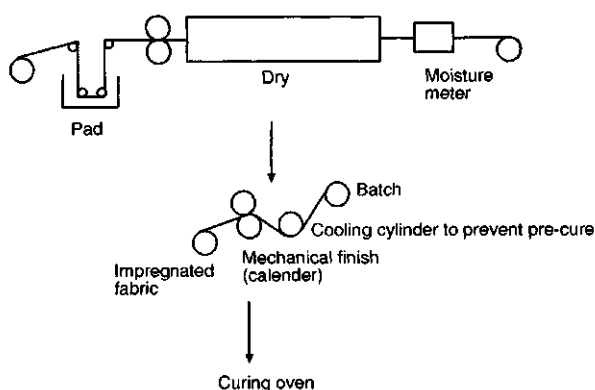
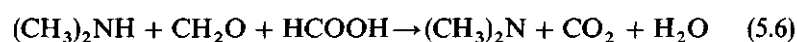
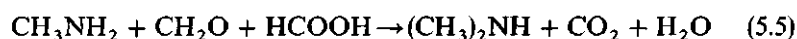
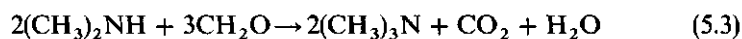
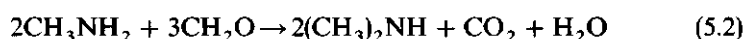
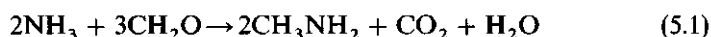


Figure 5.3 Typical layout for mechanical finishing.

unpredictable development in the fabric of a fish odour. This can occur in the baking operation but is more often associated with storage of the fabric, or with subsequent treatments involving heat and moisture such as Hofmann pressing.

In the past, the standard recommendation for preventing odour development was to wash-off the fabric after the resination process. This procedure is expensive, however, and is now regarded as unnecessary, provided that the causes of fishy odour are appreciated and adequate precautions are taken.

The fishy odour has long been attributed to the presence of methylamines in the finished fabric, and to trimethylamine in particular. The trimethylamine was said to be produced from the reaction of ammonia and free formaldehyde in the fabric, and the possibility of sodium formate being involved as well was suggested by Fluck (1951). The subject was subsequently examined in detail by Nuessle *et al.* (1959) and the significance of free formaldehyde, ammonia and formate was confirmed. Although their findings are not absolutely conclusive, they have thrown considerable light on the chemical reaction involved and have suggested that those shown below are some of the more likely (see equations 5.1–5.6).



The problem of fishy odour in fabrics may be prevented by the following.

- (1) Use of low-formaldehyde resin (e.g. the use of DMDHEU resin, which is fully illustrated in section 5.7).
- (2) Use of non-ammoniacal catalysts, although with urea-formaldehyde resins this is difficult, as the other catalysts may not have the efficiency that ammonia-based catalysts have, and are certainly not as economical.
- (3) Use of formaldehyde acceptors, such as urea or dicyandiamide.
- (4) Washing-off of the fabrics after finishing.
- (5) So-called masking agents, which one would only use as a last resort.

Other effects of easy-care finishes on fabric properties may be summarised in Table 5.1. The disadvantages may be overcome by the use of auxiliaries in the resin bath, and the following products may be employed.

For tensile strength, the addition of softeners, acrylics and preferably water-based polyurethane resin can compensate. However, the too liberal use of softeners may eventually reduce the tensile strength, and slippage of

Table 5.1 Advantages and disadvantages of easy-care finishes

| Advantages | Disadvantages |
|----------------------------------|--|
| Crease resistance, wet and dry | Loss of tensile strength |
| Improvement of shrink resistance | Loss of abrasion |
| Easy care | Loss of tear strength |
| | Slight change in shade of the dyestuff which may be due to the resin or the catalyst employed in the process |

the fibres during the test will occur. Acrylics will affect the handle and also may produce back soiling from dirty wash liquors. Water-based polyurethane resins are probably the most effective; polyurethane resins are available with glass transition temperatures as low as -60°C , thus giving very soft handles without back soiling occurring.

With regard to abrasion, softeners are recommended, but it is debatable whether the improvement of abrasion occurs due to the transference of the softener from the fabric to the abrasive material, giving a false result. In general, again water-based polyurethanes tend to give the better results, and on cotton fabrics it is possible to improve the original abrasion above that of the fabric before resin finishing. For example, with cotton rep an original abrasion figure of 20 000 Martindale falls to 16 000 with a resin finish but rises to 24 000 with polyurethane added to the resin finish.

The amounts of polyurethane solids used are relatively small, approximately 0.75–1.0% on fabric, and increased amounts give no increase in abrasion. In fact, a drop-off is noted as the amount of polyurethane is increased above the 1.5% level.

Silicone polymers and elastomers may be incorporated with resin formulations to improve the physical properties. Tests have shown that especially on polyester–cotton blends, the use of silicone-based products does give excellent results, and the amount of resin may be reduced by the inclusion of these products.

5.7 Reactant-type products

These have been on the market since the early 1960s, and the following illustration shows that the popularity of these resins has increased in proportion to the use of synthetic–cellulosic mixture fabrics. Also, it can be noted that a decrease in viscose rayon is also in proportion (Figure 5.4). The main reasons for this are as follows:

- (a) Urea–formaldehyde resins produce a stiff handle on synthetic fibres.
- (b) Urea–formaldehyde resins produce excellent crease-resistant finishes on viscose rayon with good stability and are cheap; they are still used for specific end-uses, i.e. tie linings.
- (c) DMDHEU/reactant resins do not affect the handle of synthetic fabrics and only react with the cellulosic component, thus giving a soft handle.

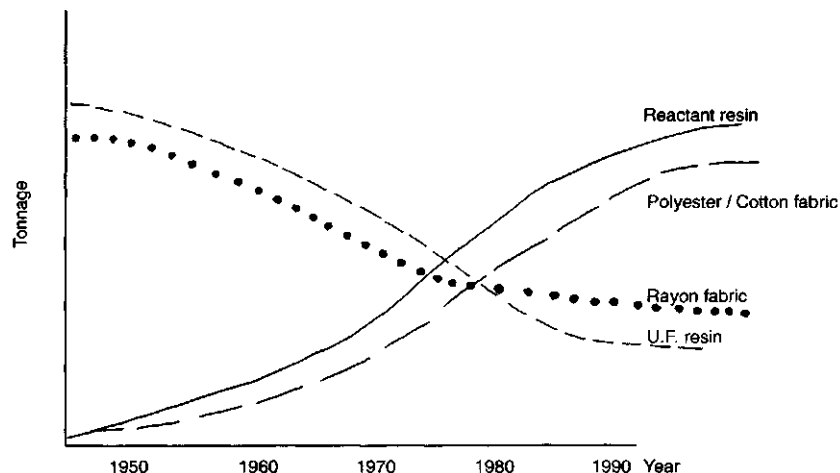


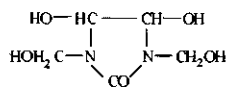
Figure 5.4 Changes in amounts of reactant resins and urea-formaldehyde resins used since 1950, together with changes in amounts of polyester-cotton and rayon used.

- (d) Urea-formaldehyde resins, in the main, give high-formaldehyde contents.
 (e) Reactant resins have a lower formaldehyde content, and they require smaller amounts of resin on to the fabric to produce results comparable with resin formers such as urea- and melamine-formaldehyde resins, again helping to reduce the formaldehyde level. Unlike older resins which form a polymeric network within the fibre, reactant products actually react with the fibre.

Reactant resins may be listed as the following:

- Ethylene urea (a) Ethylene urea-formaldehyde
 Propylene urea (b) Propylene urea-formaldehyde
 Methylated uron (c) Methylated uron-formaldehyde
 Glyoxal (d) Dihydroxyethylene urea-formaldehyde (DMDHEU)

But the most widely used product is the DMDHEU type and modifications of this. DMDHEU was introduced to replace cyclic ethylene formaldehyde resin, which was based on ethylene urea. The DMDHEU resin is based on a reaction of glyoxal, urea and formaldehyde, and reacts with cellulose by forming ether linkages under the influence of the acid catalyst.



Dimethyldihydroxyethylene urea
(DMDHEU)

Cyclic ethylene urea-formaldehyde resins (Fixapret EU; Rhonite R1 BT324)

were produced by a simple reaction of ethylene urea with formaldehyde, and came on to the market for the following reasons:

- (1) Soft handle on cotton and polyester–cotton
- (2) Good chlorine resistance on white fabrics if fully cured
- (3) Soft mechanical finishes.

However, the disadvantages of ethylene urea–formaldehyde resins were high price, and the fact that they required a full cure case to close the ring structure, in order to obtain full resistance to chlorine and prevent HCl being formed on impregnation with chlorine. These two disadvantages made the way open for new products.

Propylene urea–formaldehyde (Fixapret PHS BASF) produced excellent chlorine-resistant finishes, and the amount of cure had no effect on the finish result (i.e. non-yellowing of the finish when subjected to chlorine-containing wash liquors). The product, although expensive, filled the ‘niche’ market for the type of finish. The majority of these products are used in the production of white collar interlinings, and fabrics that would be used in the work-wear market and will possibly be subject to chlorination and laundering in the ‘hot-box system’.

5.8 Formulations for use of propylene urea–formaldehyde resin

White collar interlining. Addition of a stiffener alongside the reactant resin is normally required to produce the correct handle; the one most used is polyvinyl alcohol. This product produces the correct handle but does not affect the crease recovery of the fabric; it also does not affect the chlorine resistance of the material. Other products may be used to produce a more plasticised effect, e.g. durable softeners, but again care must be taken, as the product may give a release surface to the interlining. As most interlinings go forward for coating with a heat-seal product, this obviously will produce an undesirable effect. One product used successfully as a plasticiser is a melamine–stearamide softener (BT 323 (BIP) PERMFEL B (ACC)). This tends to give the softer handle required, but also gives a ‘Velcro’ effect to the coating. (Key Coating.)

1. Interlining finish stiff

| | |
|--|------|
| Cotton pick-up | 75% |
| Propylene urea–formaldehyde (50% solids product) | 80 g |
| Low-viscosity high-solids polyvinyl alcohol | 30 g |
| Magnesium chloride hexahydrate | 10 g |
| Water to 1 litre | |

To give a fuller softener effect, 10–20 g/l of melamine–stearamide may be added to the formulation.

| | |
|--|------|
| 2. Work-wear — 50/50 polyester–cotton | |
| Pick-up | 65% |
| Propylene urea–formaldehyde (50% solution) | 50 g |
| Silicone micro-emulsion | 10 g |
| Magnesium chloride hexahydrate | 6 g |
| Water to 1 litre | |

Alongside the propylene urea–formaldehyde resin came the heterocyclic crosslinking agents based on melamine. These are made by a reaction between ethylene urea and melamine. Examples are Aerotex 23 special ACC; BT 328 — BIP; and Lyofix NC — Ciba-Geigy. Together with the propylene urea–formaldehyde, these products held the white fabric market for a number of years.

However, the swing away from these types of resin came about with the advent of the DMDHEU, which produced similar results (with the exception of chlorine resistance) at a lower cost.

DMDHEU resins are produced by all the major chemical suppliers and are produced by a reaction of glyoxal, urea and formaldehyde. The proportion of glyoxal is high in the formulation of the resin, and therefore the price of the resin is controlled by the market price of glyoxal. Initially, unmodified DMDHEU resins were produced at 40–42% dry solids, the best-known product being Fixapret CP (CPN) BASF. However, higher-solids resins were requested from the market, and the resin solids of these products were increased to 62–65% dry solids. Various modifications of these resins are now produced, and the complexity of these are seen in Petersen (1984).

Probably the most widely used DMDHEU resins are now the low-formaldehyde versions of DMDHEU. These have been modified to produce a low-formaldehyde resin by using diethylene glycol as a formaldehyde acceptor. The formaldehyde figure can be reduced by approximately 50%, compared with the original DMDHEU resin.

Typical formulations for finishing with DMDHEU are as follows:

| | |
|---------------------------------|--------|
| Polyester–cotton 50/50 | |
| Pick up | 55–60% |
| 40% DMDHEU resin | 60 g |
| Silicone softener | 10 g |
| 40% magnesium chloride solution | 25 g |
| Water to 1 litre | |

When using low-formaldehyde resins, care should be taken with regard to the solids of the product, owing to the fact that they may have been modified with diethylene glycol. As this is 100% solids, the active solids of the product

may be lower than estimated, i.e. the cured resin solids could be as much as 25% lower than the figure obtained on evaporation of resin.

The use of formaldehyde has for some time come under closer scrutiny leading to zero formaldehyde finishes, e.g. polycarboxylic acids, being developed. However, the performance of such finishes is generally either poorer and/or more expensive to achieve.

5.9 Solids of resins

All resins have two solids values. Examples are given in Table 5.2.

(a) *Calculated solids.* This value is the solids of resin that is available for reaction in the finishing process. This may take the form of formaldehyde or free methanol, but calculating the amount of resin to treat the fabrics is difficult, owing to the fact that the amount of reactable product varies so much from product to product.

(b) *Cured solids.* This value is much preferred, and is found by heating the resin for 3 h at 120°C. The test is usually carried out on a 20 g sample of resin in a metal dish. The total solids value is the difference between before and after 3 h at 120°C (BS 2782).

There are a number of exceptions to the rule; these are normally where resins are sophisticated types of reactant such as a Fixapret AC (BASF) and BT350 (BIP).

Where the resins contain reaction products which couple with the cellulose, these products will react at low temperatures and sublime, and therefore it is necessary to carry out a solids determination at lower temperatures, e.g. 70°C for 2 h, to obtain a correct figure.

Table 5.2 Examples of solids values

| | Calculated | Cured |
|-------------------------|------------|-------|
| Melamine resins (BT336) | 80% | 72% |
| Urea resins (BT322) | 50% | 42% |
| DMDHEU (BT733) | 48% | 40% |

Table 5.3 Recommended amounts of solids to apply to fabrics

| | Urea | Melamine | Reactant |
|-------------------|-----------------|----------|-----------|
| Cotton | 6% | 4.5% | 2.5–3.0% |
| Polyester–cotton | Not recommended | 2.5% | 1.5–1.75% |
| * Viscose rayon | 8–15% | 6–9% | 6–8% |
| Polyester–viscose | Not recommended | 5% | 5–6% |

* On certain types of viscose, e.g. tie linings, an exceptional amount of resin is required.

The approximate amounts of solids to apply to the textile fabric are illustrated in Table 5.3. These amounts will give a good easy-care finish, and a stable finish to the fabric when fully cured. To obtain a good cure it is essential to take into account the following considerations:

1. That all resins require acid conditions to carry out a cure.
2. That the fabric should be fully dried before applying the resin.
3. Correct drying should be carried out.
4. The correct catalyst and amount should be used.

1. Preparation of the fabric. Before resin finishing, the fabric should be completely desized, and after bleaching, printing or dyeing, the fabric should be of acid or neutral pH. It is suggested that in the last rinse-off of the fabric prior to resin finishing, acetic acid be added in order to ensure an acid or neutral pH.

2. Padding of the fabric. It is very difficult to access the amount of resin applied to the fabric if the fabric is wet before padding. Therefore the fabric should be fully dried before padding.

3. Drying of the fabric after application of the resin. The amount of liquor applied to the fabric should be as low as possible. Therefore the mangle expression should be low, i.e. pressure on the mangle should be high.

If the fabric containing the resin is dried at an initial high temperature, the resin will migrate to the surface and give a harsh handle. For example, with a five-bay stenter the first compartment should be at 100–120°C, then the second compartment at 130–140°C, and the third, fourth and fifth may be increased to 170–180°C. This will prevent migration, and the resin will dry in the correct part of the fabric.

The use of drying cylinders for complete drying of resin-treated fabrics is not recommended; they may be used to take off initial moisture but not for full drying, as this again will give surface migration and a harsh handle will be obtained.

Table 5.4 Possible catalysts for various resin systems

| | Urea | Melamine | Reactant |
|---|------|----------|----------|
| Ammonium chloride | Yes | Yes | Yes |
| Monoammonium dihydrogen phosphate | Yes | Yes | No |
| Ammonium sulphate | Yes | Yes | No |
| Zinc nitrate | Yes | Yes | Yes |
| Magnesium chloride | No | Yes | Yes |
| Amine hydrochloride | No | Yes | Yes |
| Modified MgCl ₂ catalyst (flash catalysts) | No | Yes | Yes |
| Ammonium thiocyanate | Yes | Yes | No |

Table 5.5 Amounts of catalysts required, as % of total solids

| | Urea | Melamine | Reactant |
|--|------|----------|----------|
| Ammonium chloride | 2% | 2% | — |
| Monoammonium dihydrogen phosphate | 2% | 2% | — |
| Ammonium sulphate | 2% | 2% | — |
| Magnesium chloride (anhydrous) | — | 10% | 10% |
| Amine hydrochloride | — | 15% | 15% |
| Modified MgCl ₂ catalyst (flash catalyst) | — | 12% | 12% |

4. *Catalyst.* Table 5.4 illustrates the possible catalysts that may be used for various resin systems. It is suggested that, even though zinc nitrate is an excellent catalyst, it is ignored as it produces adverse effects on optical brightening agents.

With the advent of flash catalyst systems, such as Condensal F.B (BASF), on the market, these have been able to increase the speed of cure. They have been used mainly on cotton–polyester blends of fabric. The flash catalyst systems should be avoided on mechanical finishes, as these tend to give 'pre-cure', giving a poor mechanical effect.

Ammonium-based catalysts should be avoided when used alongside high-formaldehyde resin, because of the possibility of amine-type odours.

The amount of catalyst applied to the resin varies with each type of resin, and Table 5.5 illustrates the amount of catalyst calculated on the total resin solids. Note that MgCl₂ is normally sold in crystal form as MgCl₂ · 6H₂O, and therefore approximately 18% of MgCl₂ · 6H₂O should be used on 100% solids.

Registered trademarks

Fixapret — BASF

BT (BEETLE)—BIP Speciality Resins Ltd.

Aerotex — American Cyanide Co.

Rhonite — Rohn and Haas Co.

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