

SYNTHESIS REPORT

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TITLE:

DEVELOPMENT OF HIGH PERFORMANCE ISOCYANATE-FREE POLYMERS FOR
NEW LOW TOXICITY PAINTS

PROJECT

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ABSTRACT

New alternative isocyanate-free class of paint, aimed at replacing the high performance systems have now become necessary for mass transport applications, in order to obtain the double environmental advantage achieved by:

- the removal of isocyanate,
- the reduction in emission of volatile organic compounds (VOC).

Based on a new chemistry using the chemical reaction between anhydride tipped acrylic and hydroxylated backbones, new polymers (high functionality, low or medium molecular weight) have been developed as an alternative to the typical isocyanate-hydroxyl polymer (polyurethane) commonly used.

The target of lowering the VOC leads to the polymer weight optimisation e.g., the bimodal concept (high and low MW), by the use of

New systems have been produced and selected on the basis of the assessment of the polymers in terms of performance (crosslink density, glass transition temperature) and assessment against selected specifications and predictive toxicity.

The best polymeric system has been used for further development of a whit glossy paint: which has been tested in terms of sprayability and toxicity. Performance was then assessed against specification.

This document presents the general organisation of the project and the main characteristics of the novel polymers and paint developed, which show good properties for polymers and clear coats. The developed paint is acceptable for the majority of the tests, but has an insufficient crosslinking density as shown especially by a poor fluid resistance.

Keywords: Isocyanate-free polymers - Tipped Anhydrides - Polyols - Polymers - Clear coats - Isocyanate free paint - White paint - Materials characterization - Toxicity - Thermal - mechanical - resistance behaviour.

I - GENERAL

I.1 - INTRODUCTION

The protection of materials and structures used in the chemical industry and in transportation (railway, automotive and air) requires the use of high performance ir-drying paints. At present, only two component polyurethane paints meet the demanding requirements laid down in the specification sheets of the various users.

However although the chemical resistance, mechanical properties and weathering resistance of two component polyurethane paints are well established and significantly higher than those of other types of paint, polyurethane system have nevertheless three major drawbacks:

- one of the two components is an polyisocyanate containing about 0, 5% of highly toxic and volatile monomer,
- the level of Volatile Organic Content (VOC), especially aromatic, is very high as it is in the range of 850 to 750 g/L
- curing process and storage stability are affected by moisture.

Although no European legislation has yet been agreed to fix the maximum isocyanate level allo-

wable in the workplace, several European countries aim at reducing and strictly controlling the use of isocyanates through national regulations. The United Kingdom, for example, has already laid down an average maximum concentration of 0.02 mg/m³ for an eight hour exposure.

Moreover, reducing the emissions of volatile organic compounds into the atmosphere has become a major concern on a worldwide scale. The paint industry represents the third largest source of such emission (after power generation and transportation). It is therefore the subject of various proposed regulations and VOC control. The United States have an edge on Europe as far as the maximum levels of organic solvents are concerned (340 g/l for primers and 420 g/l for top coats). Europe is however expected to move towards these requirements in the short term

In order to find alternatives giving similar high performance protection, three different ways may be explored:

- improvement of the surface treatment,
- decrease of the susceptibility of the substrate itself using other metallic or non metallic alloys,
- modification of the paint chemistry.

It appears that the development of new paints based on isocyanate free chemistry is the more attractive choice to maintain the level of protection and to satisfy the regulations on VOC particularly when the other solutions are impossible (car refinishing, large external surfaces, decorative paints).

I.2 - OBJECTIVES

The objective of the project was to find and develop a new class of paint aimed at replacing high performance polyurethane systems which would give a double environmental advantage achieved by:

- removal of the toxic isocyanate components,
- reduction in emission of volatile organic compounds.

At the start of this research, the objectives envisaged for the paint formulations made from the novel polymers were as follows:

- high performance properties: equal or better than current polyurethane systems, that is:
 - a) Very high gloss retention (more than 85% after 1500 hours of UV irradiation).
 - b) Very good chemical resistance (300 hours in contact with synthetic fluids without degradation).
 - c) Very high flexibility even at 0°C [180° in bend test $\phi = 3\text{mm}$],
- low volatile organic content (VOC): the expected VOC is not more than 420 g/l (30% below that met in current polyurethane systems),
- low toxicity level, as widened by a target LD₅₀ = 10000 ppm, a level 1 000 times better than the typical value for isocyanate components of polyurethane systems.

The programme was divided in two main phases:

- A: a) Develop new ambient curing candidate polymer based on the chemical reaction between anhydride and hydroxylated groups born by an acrylic backbone.

The characteristics of the new polymers would be analysed

- b) screening them for **toxicological impact** using predictive computerised assessment.
 - c) Developing **precompetitive low Volatile Organic Content paint formulations**, evaluating them against specifications (railways, aircraft, industry).
- B:
- d) **Scaling up** the polymers.
 - e) **Confirming the application properties, development of paint formulations** and optimisation in respect with an **assessment against the specifications**.

1.3 - ECONOMIC POTENTIAL, INDUSTRIAL AND ENVIRONMENTAL BENEFIT

Our research, based on the chemistry patented by COURTAULDS [partner 2] defied later is focused on two parameters. The combination of both will permit a reduction of overall paint toxicity and solvent level keeping the high performance level constant. These two parameters are:

- a **new chemistry based** on the chemical reaction at room temperature between anhydride and hydroxylated polymers,
- a **high solid concept** which will permit a reduction of the VOC of about 90-40% compared with the VOC in currently polyurethane paint.

Published estimates indicate that 150,000 tonnes of polyurethane paints are used in the EC each year, with an annual growth rate of about 10%. They are sold in a variety of markets, such as Transport, Car Refinishing, Chemical Industry and Aerospace.

Published studies also indicate that about 100,000 tonnes a year of solvents are emitted from polyurethane paints in Europe.

If the projected decrease in volatile emission is achieved by the polymers for spray applied paint, solvent emissions of at least 40,000 tonnes a year could be reduced in Europe.

1.4- MEANS USED TO ACHIEVE THE OBJECTIVES

The means to achieve the objectives of this project were mainly based on:

- **the existence of an original management scheme (several tasks included in iterative loops) and of the organisation of the project,**
- **the creation of a consortium,**

which both allows exploitation of the individual competence of each company involved and enables to implement the corresponding and necessary technical resources and manpower with a continuous feed-back to all the other partners.

L4.1 - Existence of an original management scheme and organisation of the project

AS the development of new products involves not only the design and synthesis phase but has also to consider the processing potential, the possible handling of the products (toxicity), the use of the products throughout their life-cycle including the disposal and destruction phase. The structure of the project has been organised to consider all these main phases.

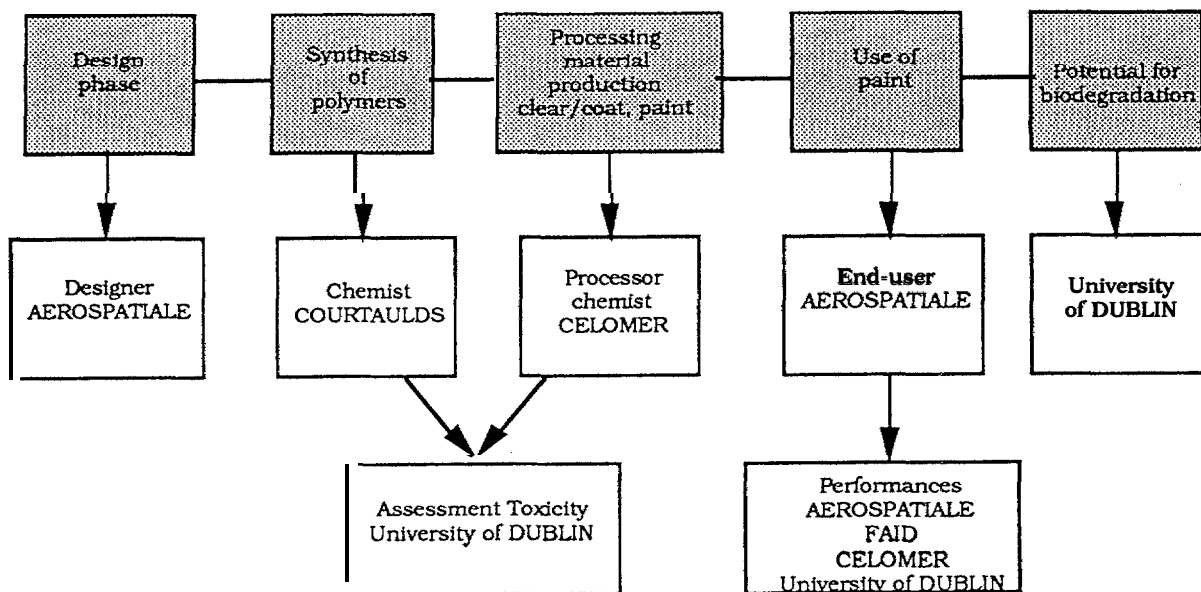
L4.2 - Creation of a consortium

To investigate and assess this new concept of isocyanate-free paint, a consortium has been formed around AEROSPATIALE under the Authority of EC - DG XII.

The goal was to develop new materials polymers → clear coat → paint] which comply with railway and aerospace requirements as well the actual and future health and safety regulations and other trends.

Following evaluation of the development and assessment of new isocyanate free paints the solution may lie in using these materials in aeronautical, building and even in other industries, i.e., railways field.

Basic life cycle of a paint



Partners involved are, in alphabetical order:

- **AEROSPATIALE:** Aerospace constructor (Partner 1).
- **CELOMER:** Paint manufacturer (Partner 3).
- **COURTAULDS COATINGS:** Synthesis, characterization and formulation of new polymers (Partner 2).
- **FAID Anticorrosione:** Paint user; technical assessment [e.g. sprayability] (partner 4).
- **University of DUBLIN:** Toxicity assessment of chemicals and materials (Partner 5).

The organisation of the research is described in the Part II (scientific and technical description of the project).

II - PROJECT DESCRIPTION

II.1 - SCIENTIFIC AND TECHNICAL PROJECT DESCRIPTION

The objective of this research was to develop a novel polymer system capable of forming the basis for formulating a high solids, ambient curing paint.

Such a paint would have a low level of volatile organic components, and being isocyanate free, would offer improvements to the user and general environment whilst giving physical and mechanical properties equal or better than current polyurethane based high performance coatings.

The three major components of paints are:

- **polymers:** forming the basis of the film and giving it chemical resistance.
- **solvents:** allowing the control of viscosity and application rheology.
- **pigments:** giving colour and other optical properties.

Each of these constituents can contribute to environmental concern in a paint.

This research was focused on polymer and solvents since pigments are already the subject of intensive research. It is possible to envisage isocyanate free high performance paint systems but with current knowledge, it is not possible to remove organic solvent completely. The target of the programme therefore is to develop polymers of appropriate structure and functionality such that:

- isocyanate systems were completely replaced by a new type of polymer chemistry,
- the organic solvent content was reduced to the minimum level necessary for application using the low VOC concept.

COURTAULDS Coatings has developed a very promising new chemistry based on anhydride derivatives.

The starting point for the new polymers was:

- a linear and branched acrylic backbone,
- on to which was attached the functional groups (anhydride on one component, hydroxyl on the other from the new chemistry presented above).

This research aimed to reconcile the low molecular weight requirements (high solids and chemical resistance) with the high molecular weight requirements (mechanical durability and flexibility) by developing polymer networks with two peaks in their molecular weight distribution (bimodal).

Once obtained, these polymers were characterized with appropriate physical and mechanical techniques.

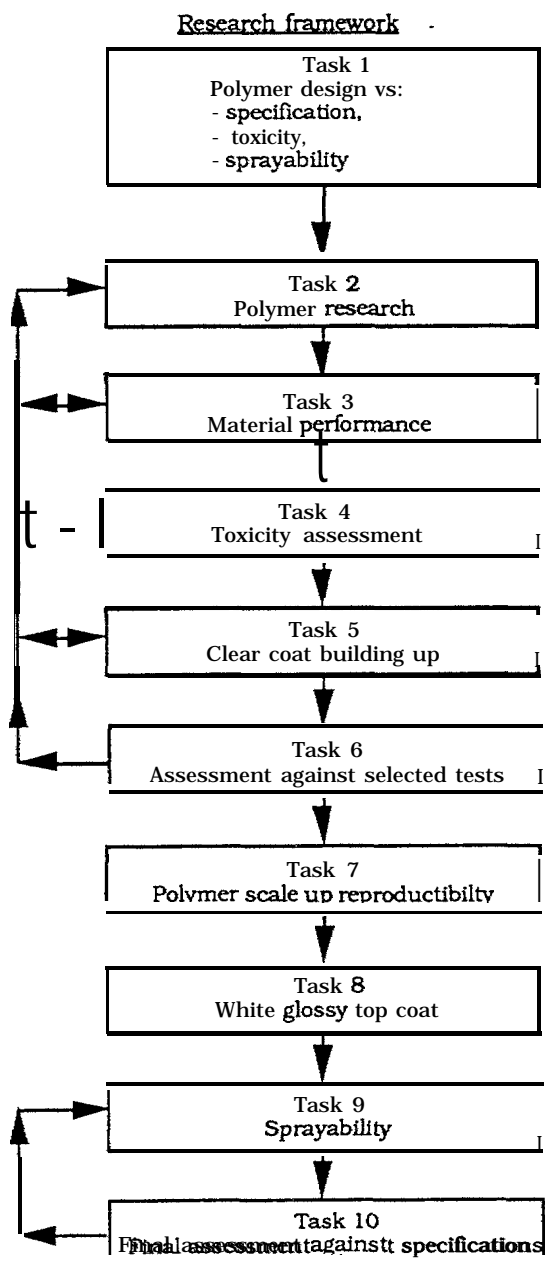
The toxicity of the product was evaluated from published data and partly by predictive computer technique TOPKAT programme.

Validation of the predictions was carried out by MICROTOX™ and MUTATOX™ methods.

The final phase of the research consisted of optimizing the polymers using an experimental clear coat and then a development formulation of one white glossy paint.

II.2 - RESEARCH PROGRAMME (ORGANISATION OF THE STUDY)

The progression of the work task by task together with the interaction between the tasks is laid out in tabular form in the flow chart below.



The main steps for the development of a new material were:

- the definition of the polymer development from the design to the assessment of the clear coat against selected tests,
- the description of the different loops (from task 2 to task 6) to develop and optimise new polymers for clear coats, followed by the selection of one or two of the best developed systems,
- the development of a paint based on the previous formulation and final assessment.

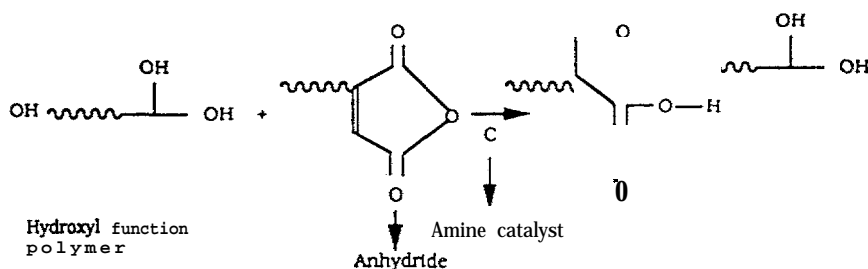
For each step, all the necessary characterizations and assessments were performed each product developed.

III - DEFINITION OF POLYMER DEVELOPMENT

The polymer development has been carried out according to the following steps described in this paragraph 3:

- 1- Polymer design.
- 2 - polymer research,
- 3- Material performance,
- 4- Toxicity assessment,
- 5- Clear coat building up,
- 6- Assessment against selected tests.

This polymer development is based on successive and iterative loops which permit rapid verification of the polymer to meet its target. The overlapping between the different tasks defined in phase I (tasks 2 to 6) becomes more and more important, the technical results of each loop are presented in section 4.



In summary, three main components are involved in the formation of the polymer:

- Anhydride,
- Hydroxyl functional polymer,
- Amine catalyst.

III.1 - POLYMER DESIGN

The main characteristics required for the polymer have been described above (paragraph II.1).

III.2 - POLYMER RESEARCH

III.2.1 - Basic chemistry

Current standard system is:

Isocyanate functional polymer + Hydroxyl functional polymer

↓

Polyurethane cross-linked coating

The approach to replacement of isocyanate containing materials is as follows:

Anhydride functional polymer + Hydroxyl functional polymer

↓ amine catalyst

Polyester cross-linked system

This is shown schematically below.

The film properties of the coating are influenced by changes in:

- (a) Type of anhydride end group
- (b) Structure of anhydride polymer backbone
- (c) Functionality of anhydride polymer
- (d) Structure of hydroxyl polymer backbone
- (e) Functionality of hydroxyl polymer
- (f) Type of catalyst

The synthesis of anhydrides according to the final polymer requirements was the major area of development.

III.2.2 - Anhydrides (hardeners)

Anhydride raw material were chosen from 7 basic typical anhydrides (e.g. maleic, himic, succinic, methyl nadic) or blends of them.

A range of materials with molecular weights in the 300-700 range and a series with molecular weights from 1000-10000 have been synthesised. The blending of similar functional polymers differing only in molecular weight to give bimodal networks was a key objective of this task.

In accordance with the requirement of high chemical resistance, the maximum amount of high molecular weight anhydride polymer was fixed at 5%.

The above syntheses and blends gave anhydrides with the requirements defined in the polymer design, i.e., functionality at least of 3, $M_w \geq 1000$.

22 anhydride polymers referenced from B001 to B022 have been developed for the study and are detailed in section IV.

c) Secondary hardener

To improve the crosslinking, a secondary hardener was tested in some loops, in order to link the free and unreacted secondary carboxylic groups released by the opening of the anhydride rings.

The main secondary hardener used was zirconium propionate (B200) which acts both as secondary crosslinking agent and also as blocking agent.

III.2.3 - Polyols (Hydroxyl function polymers)

Four commercial hydroxyl function polymers, with high functionality and medium MW have been used as basis of the polymer system B 100 (Tone 305), B101 (QR1269), B 102 and B103.

As reference, two other less functionalised hydroxyl polymer, involved in typical polyurethane were also tested: B104LH and B105LH.

The main characteristic of these polyols is:

- OH equivalent: 150 to 300 g/mol for B 100, 101, 102 and 103.

III.2.4 - Catalysts

The mainly used catalysts used were tertiary amines at levels of 2 or 3%.

III.2.5 - Characterization of prepolymers (partners 2 and 1)

The following properties were assessed:

- molecular weight : average MW and distribution (GPC).
- functionality and distribution (NMR, IR).
- T_g (DSC or DMA).
- colour, viscosity, volatility.

III.3 - MATERIAL PERFORMANCES

Checked as free varnish film by mixing base and hardener in different ratios (optimisation of formulations). The following properties were assessed.

III.3.1 - Cure extent and cure rate:

Cure schedule (time temperature), kinetics (IR, DSC), characteristics of the clear coat (task 5-6, partner 3).

III.3.2 - Cure film mechanical properties:

Glass transition temperature: T_g (DSC, DMA), **DMA:** linear expansion, elastic modulus, T_g , tensile, swellability.

III.3.3 - Durability (uv test, chemical structure ageing by IR)

III.4 - TOXICITY ASSESSMENT (Task 4, partner 5)

This was intended to deal with the initial survey of the probable toxicities of the candidate chemicals to be used for isocyanate-free polymers.

Ten basic chemicals have been examined for their potential toxicity using prediction (TOPKAT), 11 parameters of toxicity or ecotoxicity have also been examined.

The results do not suggest that there will be any extreme hazard or risks from the ten substances studied.

III.5 - CLEAR COAT FORMULATION AND ASSESSMENT (task 5 and 6, partner 9)

III.5.1 - Clear coat formulation

This task requires:

a) Choice of solvent blends according to:

- the volatility parameters,
- the sprayability characteristics,
- the flash point ($> 21^\circ\text{C}$),
- considerations of toxicity.

b) Optimisation of the **catalyst level:** pot life > 8 h and tape time = 7-9 h (23°C - 55 RH).

c) Confirmation of volatility of the polymer in each solvent separately in the blend.

d) Definition of the process to obtain a good quality clear coat.

III.5.2 - Assessment of the clear coat

The assessment of the clear coat involved 14 tests related to:

- the varnish itself: pot life, drying time, masking time and film aspect,
- the properties compared to the specifications (and a typical polyurethane reference PU 66) given in table 1.

TABLE 1

Description of tests for assessment of the varnish

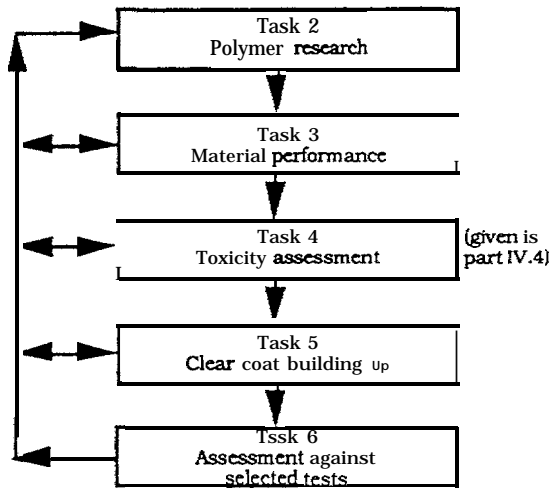
| N° | TESTS | CONDITIONS | SPECIFICATIONS | REF PU 66 | SYSTEM | AMOUNTS OF PANELS | TYPE OF PANELS |
|----|--|--|---|-------------------------------------|------------------------------|-------------------|----------------|
| 1 | POT LIFE AF 2,5 VISCOSITY AT 0, 1, 2, 3, 4 H | 23 ± 2°C 55 ± 5 % RH | BROUGHT TO 42 S MAXI 70 S AFTER 4H | 42 S AFTER 4H | LIQUID | - | - |
| 2 | DRYING FLOW TIME CLOSE OF FILM HARD ON POINT | 23 ± 2°C 55 ± 5% RH (ASN B 70 452 SP) | 10 - 45 MM 1-2 H | - 1H30 2H30 | VARNISH | 1 | DRYING BAR |
| 3 | MASKING TIME | 23 ± 2°C 55 ± 5% RH | 6-8 H | 7H | VARNISH | 1 | BIG PANEL |
| 4 | FILM ASPECT | | DRY | SMOOTH NO BUBBLING OR POPPING | VARNISH | | |
| 5 | ADHESION (G + s) | NT 10 113 | 100% | o | P99 + PAC33 + VARNISH | 1 | PANEL |
| 6 | FLEXIBILITY (NT 10 113) | 02 MM, 180° | TOTAL | TOTAL | | | |
| 7 | CLEMEN HARDNESS | NT 10113 | > 1 500 G | 3303 | " | 1 | PANEL. |
| 8 | MEK RUBS | 50 =>/<= | PAC 33 NOT VISIBLE | OK | | 1 | PANEL |
| 9 | IMPACT (DIRECT + INVERSE) | 1 KG/1 M | IC GRADE 2 | 1 | | 1 | PANEL |
| 10 | LOSS | GARDNER 60°C | >90 (/1020) | 94 | P99 + PAC 33 + VARNISH | 1 | PANEL |
| 11 | DISTILLED WATER | 14 DAYS, 20°C | CLEMEN > 1 200 G | > 1 200 | " | 2 | PANEL |
| 12 | SKYDROL LD4 | 14 DAYS, 20°C | CLEMEN > 1 200 G | >1200 | | 2 | PANEL |
| 13 | SKYDROL LD 4 | 14 DAYS, 70°C | CLEMEN > 1 200 G | LOOSENING | " | 2 | PANEL |
| 14 | QUV RESIS- TANCE (SOME SYS- TEMS) | CLOSS GARD - NER 60° | | + 5% | P99 + PAC 33 + VARNISH | 1 | PANEL |

The aspects of spray ability and assessment against film specifications are obviously included in this task:

- the sprayability and application conditions have been determined by partner 3 to prepare samples necessary for tests from N°2 to No 14, the assessment against specifications (Aircraft and Railways) are included in the 14 previously described tests, and reported later for the final assessment of the paint.

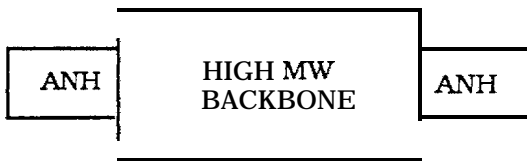
IV - LOOPS FOR VARNISH POLYMER DEVELOPMENT

The description of the main steps of a research loop is:



Five successive and iterative loops have been achieved.

IV.1 - LOOP 1 - HIGH MW ANHYDRIDE/HYDROXYL POLYMERS

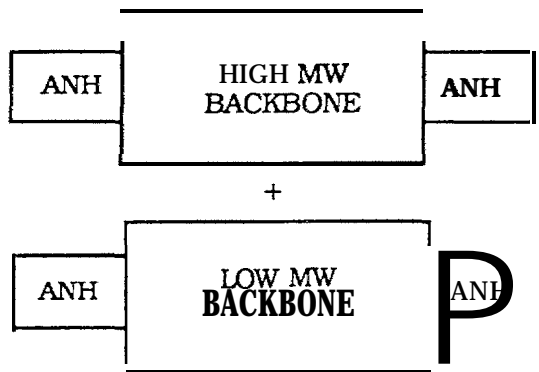


A series of 9 polymer backbones at the high end of the MW limit were tipped with anhydrides, and were formulated with 2 commercial hydroxyl polymers using a standard level of catalyst.

Films were very tacky, with low Tgs.

In conclusion, no further investigation was carried out on these high MW polymers.

IV.2 - LOOP 2 - BLENDS OF HIGH AND LOW MW ANHYDRIDE/HYDROXYL NETWORKS



a) 11 bimodal polymer blends (referenced B 1 to B 11) were prepared on the basis of:

- at least 95% mole of low MW,
 - not more than 5% mole of high MW,
- polymers tipped with anhydrides.

Polymer B6 entirely based on methyl nadic anhydride (f= 3, Mw 1 000) gave acceptable results.

b) Anhydrides reacted with 2 polyols B100 and B101 were tested (22 systems) and showed generally a low crosslink density, except for system

B6/B 100 which pass the 14 tests, except drying time is too long.

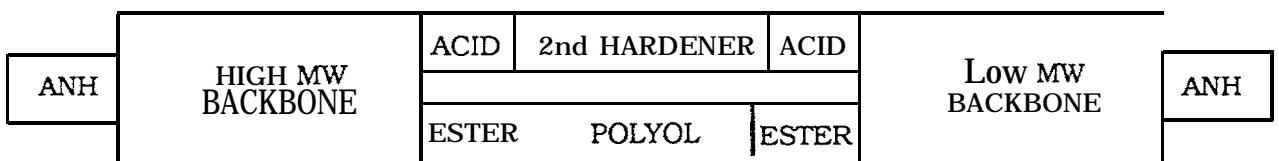
Hydrolysis was observed and decrease the cross-link density,

c) An additional kinetic study by FT-IR (in situ heating cell) on B6/B 100 system showed that no reaction occurs in 3 hours at room temperature, but a complete reaction is observed above 130°C.

This method was applied to model acid/hydroxyl system and confirmed that no reaction OH-COOH occurs at room temperature (only above 130°C).

d) Conclusion of loop 2: the best candidate of high/low MW blends is B6/B100 system which meets the specifications (except drying) time and has a medium crosslink density.

IV.3 - LOOP 3 - SECONDARY CROSSLINKER IN NETWORK FORMATION



two polymers were developed by adding to B6/B100 system a secondary hardener (B200): zirconium propionate at 2 different contents (2,5 and 5%) and were tested.

In summary:

Addition of the second hardener improve reaction time but a decrease of film hardness and skydrol resistance are observed.

Only a small amount of 2nd hardener (around 2%) is acceptable.

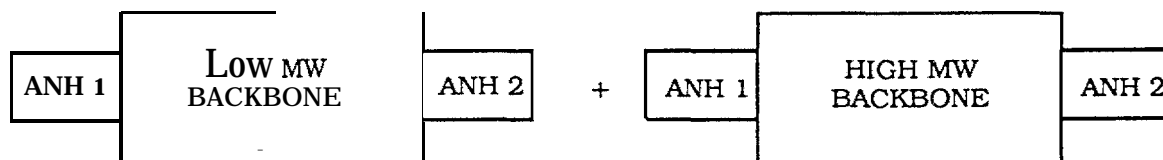
The second hardener acts at low concentration to increase the kinetic rate, but the crosslinking seems to decrease.

The main action of B200 is probably a blocking effect (and not crosslinking).

Some tests have been carried out in further loops [especially with B18/B 102 system], results are worse due to flocculation problems and at the end the use of this secondary hardener has been rejected.

IV.4 - LOOP 4 - MIXED ANHYDRIDE TIPPING

Four polymers referenced from B 15 to B 18 were developed by mixed anhydride tipping:



B15 MNA/MA 3/1 Good physics test with B 100

B16 MNA/MA 7 / 1 Good physical test with B 100

B17 HA - Poor solubility - Reactive ANH, good conversion (in tipping)

B18 HA/OCT 3 / 1 Solubility equivalent to B6
Good network, "flocculation" issue

Where:

MNA: Methyl Nadic Anhydride

MA: Maleic Anhydride

HA: Himic Anhydride

OCT: Octenyl succinic anhydride

associated with poly B 100, B 102 and B 103 (activated hydroxy polyol developed by COURTAULDS), and catalysed with a tertiary amine.

a) A first screening of 21 systems, essentially based on compatibilities with solvents to formulate a clear coat, led to six formulations:

- B6/B 100/B200 [2.3% and 4.6%],

- B15/B100,

- B16/B100,

- B18/B102 (1/1 and 1/2).

b) Tests on clear coats based on these formulations were good only for two anhydride polymers:

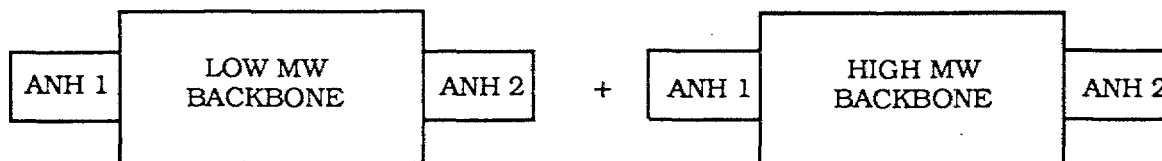
- B15: (MNA/MA 3/1),

- B16: (MNA/MA 7/1).

It appears that the combination of methyl nadic and maleic anhydrides leads to good results, and further work was completed with systems based on B 15 and B16 (loop 5).

IV.5 - **LOOP 5** - Mixed anhydride tipping (continued)

Four additional polymers referenced from B 19 to B22 were developed according the same scheme as for loop 4.



B19 HA/OCT 5/1 Improved volubility

B20 HA/OCT 7/1 Improved volubility

B21 MNA/HA 3/1

B22 MNA/MA 5/1 Intermediate version between B15/B16

associated with the 3 previous polyols: B 100, B102 and B 103 and catalysed with a tertiary amine (tests carried out with other catalysts showed a small improvement of conversion, but a green colour appeared).

a) Basic tests on materials showed that B19 and 320 had lower material performance (compared to B21 and 322) and were not selected.

b) **The complete assessment** at the end of the loops was carried out on:

1) Anhydrides

Only 4 anhydrides B 15, B16 (from loop 4), B21 and B22 were fully tested.

B 15, 322, B 16 contain maleic anhydride (MA) combined with an increasing level of MNA (methyl nadic anhydride).

B21 was developed from B 15, replacing MAN by HIMIC to improve reactivity.

2) Polyols:

5 polyols were tested:

• B100, 3102 and B103 (previously described),

• 2 additional polyols currently used in aircraft paint as references: B 104 and B 105, with lower functionality, but good Skydrol resistance when cured with isocyanates;

3) Catalyst: Typical tertiary amine (DMCD)

4) Formulations:

• anhydride/polyol: molar ratio 1/1,

• catalyst: amine /an hydride = 10%.

c) Results

20 systems were fully characterized according to the 14 clear coat assessment tests. Results of the best systems are given in table 2.

V.6 - CONCLUSION OF **THE POLYMER RESEARCH LOOP**

At the end of the five research loops, the best anhydride candidates (based on mixed anhydride tipping) are:

- B15 mixed MNA/MA 3/1,
- B22 mixed MNA/MA 5/1,
- B21 mixed MNA/HA 3/1.

Several systems based on B15 and B22 are close to the specifications (B 16 is dissolved in Skydrol and 321 do not pass MEK RUB test) especially when associated with B 100 or B 102 polymer. These systems are candidate for the final selection.

The selected system is B22/B100 meets all the specifications (especially gloss and fluid resistance) except the drying time.

For the B22/B 100 clear coat the values achieved for the most demanding tests are the following:

- gloss = 90 (spec= 90),
- water resistance = 2 500 (spec = > 1200),
- skydrol 20° = 1 400 (smooth-rivelling) (spec = >1 200),
- skydrol 70°C = > 3000 (smooth-rivelling) (spec = >1 200).
- drying time:
 - flowing time =90 min (spec 4.5 min),
 - closing of film. 4H30 (spec 2H).

V - PAINT DEVELOPMENT

Starting from the selected polymer system i.e., B22/B 100, a white glossy paint has been developed and assessed.

V.1 - WHITE GLOSSY DEVELOPMENT FORMULATION

V.1.1 - Objective

The basic formulation (weight) for this paint keeping the same ratios as for the varnish was:

- * B22 (dry part): 30-40%,
- titanium dioxide: 30-40%,
- B100: 20-W%,
- DMCD (catalyst): - 4-5%.

This formulation was adapted to achieve:

- gloss over 90%,
- good aspect,
- good applicability.

At the end, 50 l of white paint were manufactured.

V.1.2 - optimisation

- The paint ready for spraying is obtained by mixing (in weight):
 - base [(B22 (60-70%)/TiO2 (30-40%)] 100 parts,
 - hardener [B 100 (80-90%)/DMCD (10-20%)] 21 parts,
 - thinner MPA" 57 parts.
- MPA = Methoxy Propyleneglycol Acetate
- The basic formulation is too heterogeneous and not applicable without any additives, different tests of grinding led to incorporation of 4 additives in the base:
 - AD1 (wetting agent) -0.290,
 - AD2 (thixotropic agent) - 2%,

- AD3 (thixotropic agent) - 1%,
- AD5 (polar agent) - 0.5%.

- The final adjustments were made in a sandmill.
- The best application method selected: (1 simple pass + 10 min drying times applied for:
 - horizontal application,
 - vertical application on contrast card and riveted cans.

It was noticed that the gloss decreased when the content of thixotropic agent was increased.

The final optimised formulation CELOMER Code Number 9999/5680 is reported in table 3.

V.1.3 - Tests according to the specification

The formulated paint 9999/5680 was assessed against the 14 specification tests listed earlier in table 1.

The results reported in table 4, were compared to the compared specification the PU 66 reference and the varnish B22/B100 values.

In summary, the BRITE paint 5680 is below the specification on:

- drying time and masking time (but the new low VOC PU paints currently used have generally longer drying times than typical high VOC paints),
- gloss [for this batch only], other B22/B 100 batches have a gloss value over the specification (> 90),
- Skydrol at 70°C,
- * QUV resistance, but no anti-UV additive has been added in the formulation.

TABLE 3

Formulation of the white paint

1 - BASE: 999/5680

| | |
|-------------------------|---------------------------------------|
| Titanium dioxide | ≈ 30 |
| B22 (50% solids in PMA) | ≈ 60 |
| Additional solvents | ≈ 6 |
| Additives (4) | ≈ 4 |
| d = 1.491 g/cc | Solids (2 g/3H/105°C) = 67.5% |
| FP = 31°C | Fineness North = 9.5 |
| VOC = 519 g/l | Viscosity (AF 2.5-20°C) = Thixotropic |

2- HARDENER: 9999/5681

| | |
|-----------------|-----------------------------|
| B100 | -80-90 |
| DMCD (catalyst) | -10-20 |
| d = 1.040 g/cc | Solids (theoretical) = 100% |
| FP = 108°C | Finess (North) > 9.5 |
| VOC = 0 g/l | Viscosity (AF6-20°C) = 52 s |

3 - THINNER: 9999/5682

| | |
|----------------|-------------|
| MPA | = 100 |
| d = 0.968 g/cc | Solids = 0% |
| FP = 50 | |
| VOC = 968 g/l | |

MIXING RATIO (WEIGHT): Base/Hardener/Thinner = 100/21/57

APPLICATION VISCOSITY AF 2.5/20°C = 70 S

V.1.4 - Conclusions

The formulated paint CELOMER 9999/5680 does not meet all the specification requirements and gives especially an insufficient degree of crosslinking (as shown in table 4).

Apparently, the presence of titanium dioxide pigment [content 27% in paint (36% in dry paint), average size -5 μ] and probably, with a lower influence, the addition of - 2% of thixotropic agents, hinder partially the polymerization, compared with the system without additives. It would be necessary to increase the crosslinking when the pigment is present in the polymeric system.

Nevertheless, an isocyanate free paint has been developed with a good aspect and being reasonably well applicable. The VOC level has been lowered to 625 g/l (spec. 420 g/l) being still 49% over the target but lower than the results of the varnish B22/B 100: 718 g/l (71% over the target).

Further work on a non optimised top coat has shown that this VOC could be lowered to 514 g/l by using MIBK instead PMA, being then only 22% over the target. This would mean a 27% decrease of the VOC, compared to the mean value of 700 g/l of the normal VOC PU topcoats.

TABLE 4

Tests according to the specification NT 30113: white paint 9999/5680

| Test | | Specification | P99 + PAC 33 + PU66 | | | | | E22/B100 Varnish | | | | | P99 + PAC 33 + PAINT 9999/5680 | | | | |
|--|-------------------|---------------------------------------|-----------------------------|----|--|----|----|-----------------------|----|----|----|--|-----------------------------------|----|-----|-----|-----|
| CECA resistivity (kΩ) | | | | | | | | | | | | | A/B/C (weight) 100/21/57 80 kΩ | | | | |
| V(3C (g/l)) | | 420 g/l for top coat | | | | | | 718 | | | | | 625 | | | | |
| Pot life Viscosity AF2.5/23°C (S) | | No (less than 70 S after 4H for PU66) | T=0 | 1H | 2H | 3H | 4H | 0 | 1 | 2 | 3 | 4H | T=0 | 1H | 2H | 3H | 4H |
| | | | 60 | 62 | 65 | 68 | 73 | 42 | 44 | 46 | 47 | 49 | 70 | 87 | 103 | 120 | 137 |
| Film aspect | | OK | OK | | | | | OK | | | | | Quite glossy: 77% good aspect | | | | |
| Drying Time Flowing time Glose of film 20°C/55%HR Hard on point | | 10-45 mn 1-2H | OK 30mn 1H30 4H30 | | | | | 1H30 4H30 10H00 | | | | | 10 mn 6H00 10H00 | | | | |
| Masking time 23 ± 2°C/55 ± 5% HR | | 6-8H for a finish | 8H00 | | | | | > 7H00 | | | | | 20H00 | | | | |
| Clemen hardness | | > 1 500 g/metal | > 2 000 g | | | | | > 4 000 | | | | | > 2 000 g | | | | |
| Adhesion@+ S) | | 0 | 0 | | | | | | | | | | 0 | | | | |
| Flexibility 02 mm/ 180° | | Total | Total | | | | | Total | | | | | Total | | | | |
| Impact resistance B33900 F3 (1 m, 1 kg) direct | | Max grade 2 | 1 | | | | | 1 | | | | | 1 | | | | |
| Gloss gardner 60° (1/1000) | | Mini 90 | 89 (mead | | | | | 90 | | | | | 82 (mean) | | | | |
| Curing:50 MEK RUBS | | No (film not softened) | OK | | | | | OK | | | | | (Softened) | | | | |
| Distilled water 20°C | 7 days | Clemen Hardness | > 1 200 | | | | | | | | | | > 1 200 | | | | |
| | | Adhesion | 0 | | | | | - | | | | | 0 | | | | |
| Distilled water | 14 days | Clemen Hardness | > 1 200 | | | | | > 1 200 | | | | | > 1 200 | | | | |
| | | Adhesion | 0 | | | | | 0 | | | | | 0 | | | | |
| Skydrol LD4 20°C | 7 days | Clemen Hardness | > 1 200 | | | | | | | | | | > 1 200 | | | | |
| | 14 days | Clemen Hardness | > 1 200 | | | | | > 1 200 | | | | | 1403 | | | | |
| Skydrol LD4 70°C | 7 days | Clemen Hardness | > 1 200 | | | | | | | | | | Finish dissolved | | | | |
| | 14 days | Clemen Hard ness | > 1 200 | | | | | > 1 200 | | | | | Film dissolved | | | | |
| QUV 1 000H [42 days | Color Cl Lab D65 | | Color difference negligible | | dE = 1.31 dL=0.18 dA = - 0.25 db=1.27 | | | | | | | dE = 2.56 dL = 0.29 dA = - 0.87 db = 2.39 | | | | | |
| | Gloss Gardner 60° | | 68.9 (- 23%) | | | | | | | | | | 27(- 67%) | | | | |

V.2 - SPRAYABILITY ASSESSMENT

V.2.1 - Definition of materials and tests

a) Spray devices: 4, with the following conditions:

- Air Spray Gun (ASG), Air pressure 3.1 and 4.2 bars. Tank pressure 0.7 to 1.4 bars.
- Air Coat Spray Gun or Air Mix (AM). Air pressure 2.8-8 bars. Operating fluid pressure 50-80 bars.
- Airless (AL) Fluid pressure 100-150 bars. Flow delivery 0.38-0.47 lml- L
- Electrostatic Air-Assisted Airless Spray (E.A). Air pressure 21-28 bars. Fluid pressure 2.8 bars,

tested in a range of temperature from 20°C to 35°C for samples

b) Samples

Prepared for the final assessment against specifications:

- Aeronautic: 50 aluminium samples (2024 or AU4G 1 alloy), surface treatment chromic anodising, protection Primer Intergard 90,
- Railways: 20 steel samples, quality ZES: XC 18, surface treatment: decreasing and/or sand blasting.

c) Criteria for sprayability tests:

- Defects: sagging, orange peel,
- Paint DFT: Dry film thickness,
- Adhesion (ISO 4624): rupture strength (MPa) and mode of failure (adhesive, cohesive),
- Gloss (gardner).

V.2.2 - Results

A complete assessment was carried out for 4 spray devices, under 30 different conditions, on a total of 91 panels.

The criteria were ranked as follows:

- mode of failure > gloss > rupture strength > defect,
- the results (expressed in % of good results) ranked the spray devices as follows EA (90%) > AL (50%) = AM (50%) > ASG (40%),
- in summary electrostatic airless spray gave the best results;
- the different parameters do not affect the results, except the pressure (especially for Air Mix and Airless guns); quality of results (20% for AM or 100% for AL). increase with p

V.3 - FINAL ASSESSMENT

The paint 5680 was assessed against specifications and toxicity.

V.3.1 - Assessment against specifications

Tests were carried out:

- by CELOMER at the end of the development of the paint and have been reported earlier table 4, paragraph V.2.3,

- by AEROSPATIALE on samples prepared by FAID for tests of sprayability.

These last tests were carried out on samples aged for 3 months and stored at different mom temperature and relative humidities.

Tests results initially state are good except for hardness (< 600 g).

After the water resistance test, adhesion give good results but hardness is insufficient (< 800 g).

Skydrol resistance is not sufficient.

- 20°C: softening start of dissolution after 24 hours,
- 70°C: complete dissolution at 96 hours.

The last results, on aged samples show a decrease of performance compared with fresh samples. Partial hydrolysis may have occurred during storage.

This fact should be assessed by retesting in controlled conditions after, for example, ageing in a regulated humid atmosphere (NT 10113- Test 4-3-6:500 h) and checking of hardness.

In summary, the new developed BRITE 5880 paint:

- meets the specifications (except skydrol at 70°C) for fresh samples,
- shows a decrease of the crosslink density after a natural ageing (hardness, water and Skydrol resistance).

Some improvements should be made to reduce the partial hydrolysis of the paint (by blocking for example for carboxylic groups).

Note: when cured at 70°C after formulation, the paint meets all the specifications, with an improvement of all the properties.

V.3.2 - Assessment of toxicity

The final toxicity assessment was devoted to complex chemicals (formulations, mixtures, polymers which can not be assessed by the predictive toxicity programme TOPKAT).

Studies were carried out by two experimental methods: MICROTOX™ and MUTATOX™, respectively metabolic inhibition and mutagenicity on eleven chemicals used for the paint formulation.

No marked toxic hazard was detected on the components of the developed paint.

CONCLUSION

A new anhydride tipping chemistry has been developed during this three year research for the synthesis of high performance isocyanate-free polymers for new low toxicity paints. New polymers with the required properties have been obtained.

A paint based on one of these polymers has been formulated. It behaves quite satisfactorily except for fluid resistance at elevated temperatures (70°C).

Two main phases involved in the research have been completed:

A) New polymer development

These polymers are based on a new reaction chemistry for synthesis of anhydride polymers in presence of a catalyst.

- 1) More than 20 anhydride polymers including 10 anhydride bases (or blend oil) tipped on a poly-meric backbone (generally polyester) have been developed and their performances have been checked initially alone then in association with polyols. All the polymers (anhydride, polyols) have a high functionality and low average weight (Mw ~ 1000).
- 2) A predictive toxicity assessment was carried out on the anhydride bases and showed no marked effects.
- 3) More than 60 anhydride-polymers systems were prepared and fully assessed against the specifications.

The research was carried out by five iterative and progressive steps from the conception of a new polymer to the full assessment of the clear coat.

Five anhydrides (B 15, B16, B21, B22) associated with two polyols (B 100, B 102) have led to good results.

The best performance has been obtained with the B22/B100 system which meets all the requirements, except for the drying time (twice as long).

Notes: Up to double the length drying time is commonly used with new low VOC systems.

When cured at 70°C, the system meet all the specifications with an improvement of all the properties.

B) New paint development

- 1) A new paint (glossy white top coat) based on the B22/B100 system was formulated and scaled-up to 50 kg.

This new paint meets the specifications, except for Skydrol resistance at 70°C (severe test) and MEK RUBS, probably due to an insufficient degree of crosslinking.

When cured at 70°C, a large improvement in the paint properties, especially fluid resistance, is observed.

When the paint samples are stored at ambient conditions for 3 months, properties related to the degree of crosslinking are decreased.

- 2) A large screening was performed in order to optimise the spray conditions in terms of adhesion and gloss [electrostatic device appears to be the best method].

- 3) An assessment against toxicology does not show any evidence of major toxic risk on the material developed.

In summary, new isocyanate free polymers, based on a new chemistry of anhydride polymers and polyols with a high functionality and a low molecular weight, have been developed.

several clear coats were successfully formulated showing a complete agreement with the railways and aeronautical specification.

Starting from one of the best polymer systems, a white glossy paint has been developed and scaled-up successfully. The new isocyanate-free paint meets almost all the requirements of the specifications, except for properties related to the degree of cross-linking which is not sufficient for severe tests such as elevated temperature fluid resistance.

Nevertheless, the paint developed:

shows good properties when cured at 70°C and can be used for small or medium assemblies in the aeronautical or railways sectors.

is close to the objectives (aeronautical paint cured at room temperature) some additional studies would be necessary to reach the target,

is based on a binder selected among more than 20 high performance systems resulting from this new chemistry of high functionality anhydrides and polyols polymers applied to isocyanate free binders for paints. These binders (or clear coats) meet the specifications, including severe fluid resistance tests,

do not show any particular toxicological risk,

presents with some solvents a reduced VOC slightly higher than the target.

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