

## **Characterization of tannery chemicals: Retanning agents**

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### ***Introduction***

The retannage of the leather represents a very important phase in order to obtain specific characteristics, for example the fullness, on the finished product. The retannage can be carried out employing various categories of substances such as acrylic resins, dicyandiamidic resins, melaminic resins, syntans and so on.

In this work, an analytic characterization of such products has been carried out with the aim to improve the knowledge of their main components, that we find again in the finished leathers and in the emissions (wastewaters, air emissions, and solid wastes) rising from the tannery process. In particular, on such products, we have carried out both chemical analyses in order to estimate their composition and instrumental analyses (IR spectroscopy) for the identification of the “active matter”. Furthermore we have carried out analysis of free formaldehyde content of condensed products in order to evaluate the environmental impact.

### **Retanning agents**

The chrome leathers are often retanned to give the leather fullness with selective filling of the structure and to provide a tight and uniform grain surface for leather finishing.

Retanning agents can be inorganic mineral substances (chrome, aluminium, zirconium salts) or organic substances (aldehydes, vegetable tannins and syntans, resins).

There are wide differences in chemical composition. You can divide retanning synthetic organic agents in three main groups:

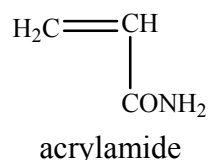
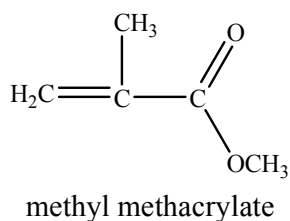
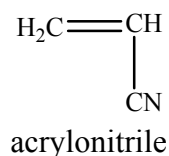
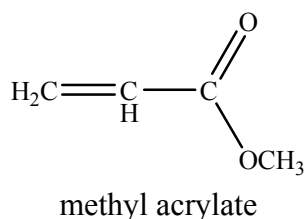
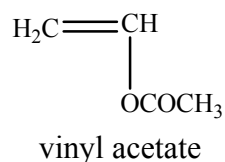
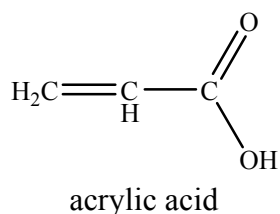
1. Syntans: condensation products of aromatic compounds like phenol, naphthalene sulphonic acid with formaldehyde or urea
2. Resins: condensation products from formaldehyde with amino and amido compounds like urea, melamine, cyanamid.
3. Polymers: mainly polyacrylics, i.e. polymerization products from acrylic acid derivatives.

These synthetics can usually be used in pretanning with glutardialdehyde, in retanning for filling and softening, as auxiliaries during fatliquoring and sometimes as replacements tannins in combination with vegetable extracts.

To produce an ovine leather for footwear, approximately 25% of retanning agents on shaved leather weight is needed and generally it's constituted of inorganic retanning agents ( $\cong 5\%$ ), vegetable tannins and syntans ( $\cong 8\%$ ) and resins ( $\cong 12\%$ ). To produce an ovine clothing leather, the needful quantity of retanning agents is lower and is approximately 15%. However, in all cases, synthetic resins have found great use: in fact in the first case (footwear) resins are above 40% of total retanning agents, in the other (clothing) the resins are 30%. The wide use is due to the presence, in most of resins, and overall in that of acrylic type, of many side carboxylic acid groups that can give tanning property both reacting with multiple chrome centers on the leather and having a chemical bound to groups of collagen. Because of large use, the study had focused principally on synthetic resins and acrylic polymer.

### *Acrylic polymers*

The products employed in tannery are homopolymer or copolymer of acrylic acid and its derivatives.



The synthesis of copolymers is obtained by free radical polymerization.

A free-radical polymerization has three principal steps:

1. Initiation of the active monomer
2. Propagation or growth of the active (free-radical) chain by sequential addition of monomers
3. Termination of the active chain to give the final polymer product.

Many free-radical reactions are conducted *in solution*. Important water-soluble polymers that can be synthesized in aqueous solution include poly(acrylic acid), polyacrylamide, poly(vinyl alcohol) but poly(methyl methacrylate) can also be polymerized in organic solvents.

Another technique that utilizes water as a heat-transfer agent is *emulsion polymerization*. In addition to water and monomer, a typical reactor-charge for an emulsion polymerization consists of a water-soluble initiator, a chain-transfer agent, and a surfactant such as the sodium salt of a long-chain fatty acid.

An example of a commonly-used water-soluble initiator is the persulfate–ferrous redox initiator, which yields a radical sulphate anion through the reaction



Type and ratio of the vinyl polymer have effect on properties of retanned leather; in fact fastness, heat stability, softness and tannage distribution depend not only from tanning agent concentration but also by distribution of molecular weight and comonomers ratio: then it's very important choose the retanning agents on the basis on these factors. By modifying the backbone composition, molecular weight and branched functional group polymers can be designed to give a specific performance. Acrylic acid is usually used in combination with acrylonitrile, acrylamide, and acrylate (esters). The acrylamide have a remarkable effect on the fullness, as the presence of amido groups gives to tanning agent compatibility with collagen fibres, resulting in better penetration and combination ability.

A comonomer that contains polar groups, such as –CN, CONH<sub>2</sub>, COOH, can increase the strength of collagen fibres. At proper ratio, it can also increase the stability to wet heat. For example the introduction of acrylonitrile into the molecule of the tanning agent can increase the tensile strength of retanned leather as it increase the combination of the tanning agent with collagen and produce more hydrogen bonds. However the introduction of polar groups harm the softness of the leather.

The introduction of acrylic ester co-monomer (i.e. methyl acrylate) into tanning agents can improve the flexibility of collagen fibres of retanned leather and the extent of the improvement depends on the length of the carbon chain in the ester group.

The copolymer with a methyl group inside the main chain, such as methylacrylic acid or methyl methacrylate, can produce a low tanning effect as it increases the distance between the molecules of

the tanning agents and the collagen. For this reason, the side methyl group in the tanning agent does also harm to the strength, softness, fullness of retanned leather and the flexibility of the collagen fibres.

### **Resins**

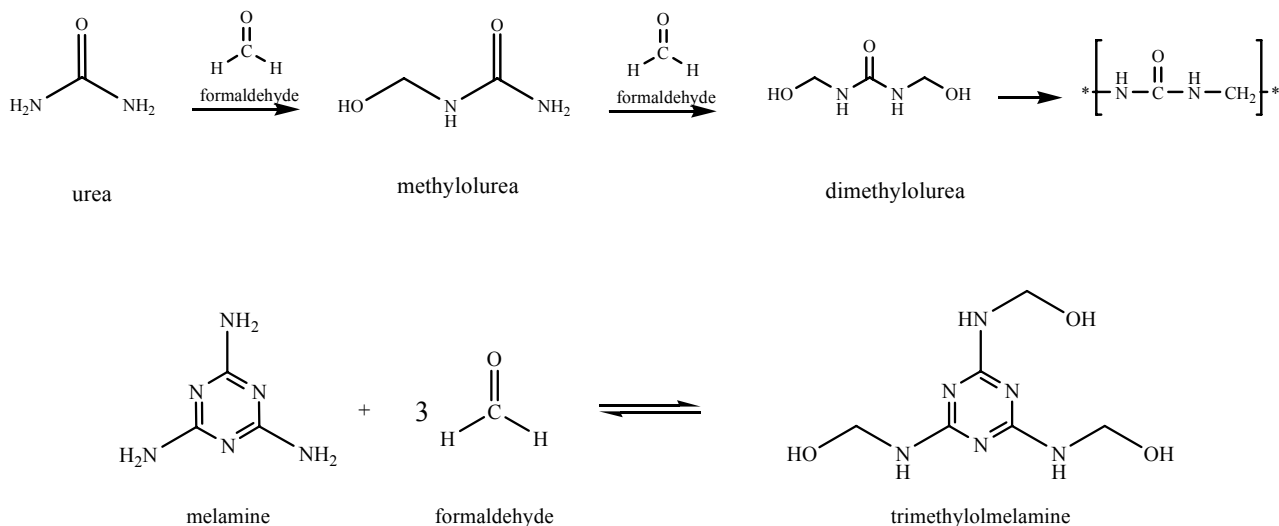
These polymers are synthesized by condensation reaction of formaldehyde with urea, melamine, dicyandiamide.

The polymers can be chemically modified to improve the affinity with collagen and to make water soluble product: therefore the polymers can be sulphited by reaction with a sulphonating agent after the synthesis or by using sulphitated monomers, like naphthalensulphonic acids, during condensation reaction.

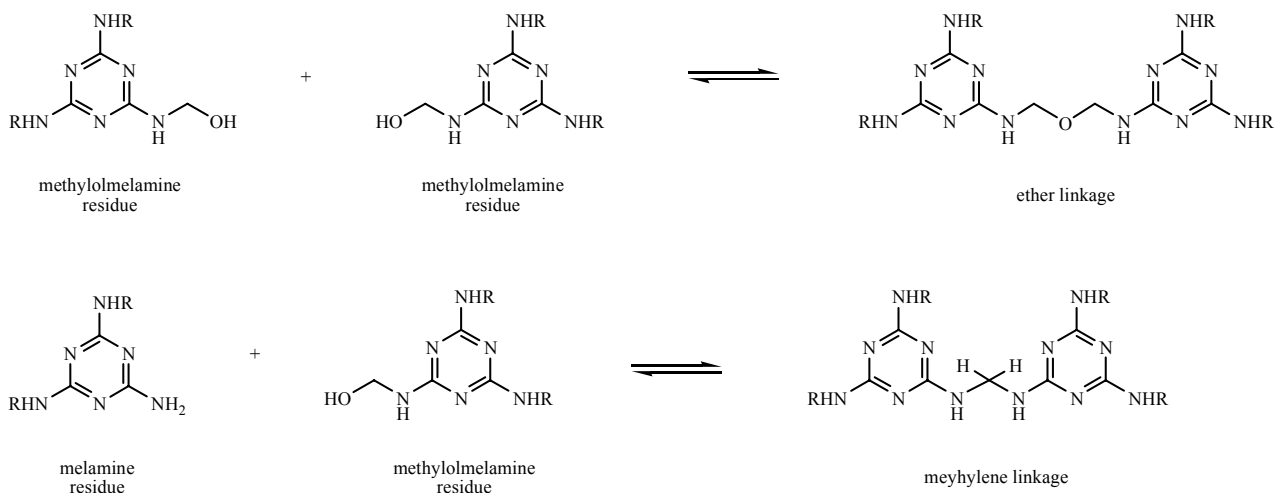
#### *Urea and melamine resins*

The amine resins usually used in retanning process are polymers synthesized by condensation of urea and formaldehyde or urea, formaldehyde and melamine (2, 4, 6- tramino- 1, 3, 5-triazine).

The formaldehyde undergoes an addition reaction with amino group of urea or melamine with the formation of N-methylol groups.

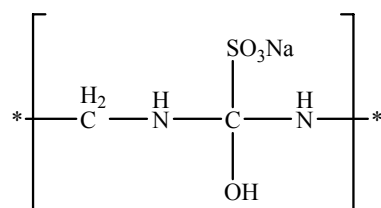


The methylol groups can react with amino or other methylol groups to form methylene or ether bridges, according to the following reaction scheme for melamine:



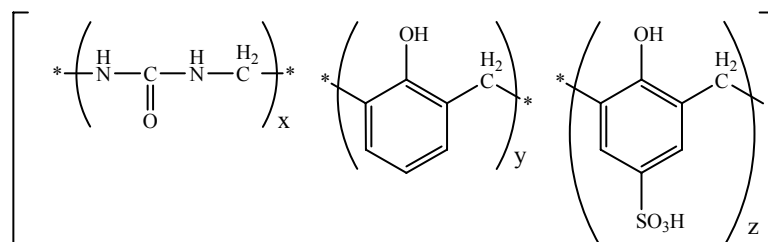
However the products obtained are determined by the mole ratio of the reactants, the concentrations of solutions and the pH. In some resins, such as MUF (melamine-urea-formaldehyde), the formation of methylene linkages is induced mainly by reaction of methylol groups of melamine and primary amino groups of urea residue, instead dimethylene ether linkages are preferred in the case of a defect concentration of urea. These resins give light coloured leathers with good resistance to degradation induced by light and are used in combination with vegetable tannins because of poor tanning capability.

Urea-formaldehyde resins can be synthesized either at alkaline (8-9,5) or acid pH (3,5-4,5) at temperature 70-100°C. The polymer can be chemically modified by reaction with a sulphating agent, generally sodium bisulphite to form a sulphonated soluble product.



Sulphonated polymeric structure

Besides urea can be introduced into phenol-formaldehyde resins to improve their curing, to lower the content of free formaldehyde and to reduce the cost of resin. In many cases, the resins can be obtained by condensation of urea, formaldehyde, phenol and phenol-sulphonic acid:

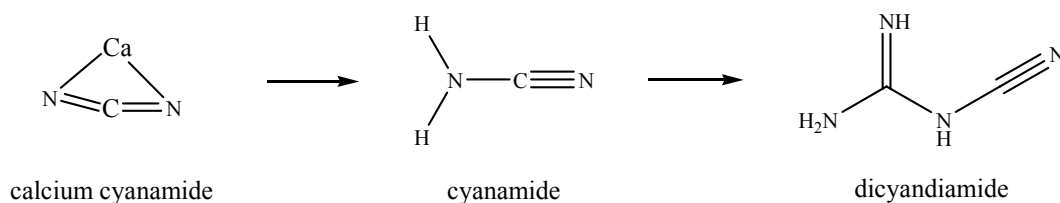


By varying the proportions of monomers, the properties of resulting resin can vary widely. In fact a too large excess of phenol respect to sulphonated monomer decrease the water solubility of resin, otherwise when the ratio between the two monomers becomes too low the tanning proprieties diminish.

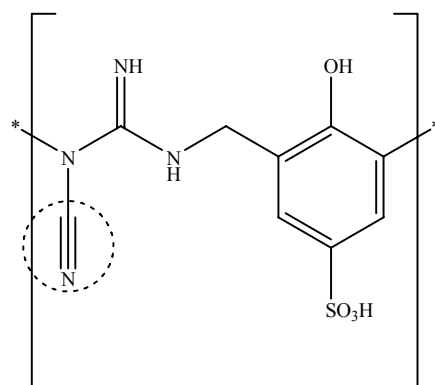
Other modified cationic resins are synthesized for reaction by organic bases such as triethanolamine or diethanolamines.

#### *Dicyandiamide resins*

Another type of resins are constituted by dyciandiamidic resin. Dicyandiamide or cyanoguanidine is produced by dimerization of cyanamide, obtained by high temperature decomposition of calcium cyanamide in acid solution:



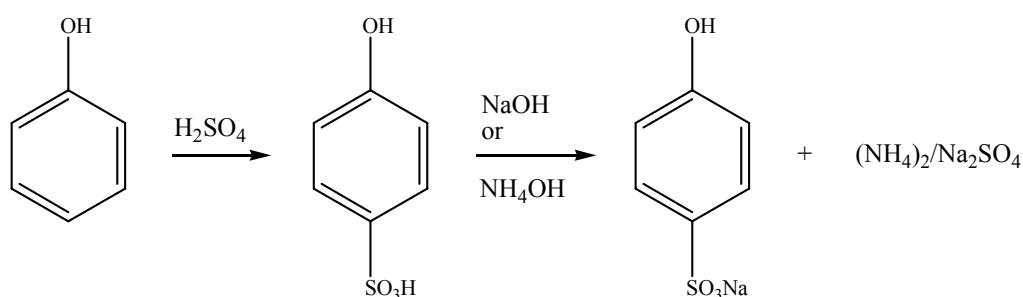
Dyciandiamidic resin are obtained from condensation between cyanoguanidine and formaldehyde or urea and can give further condensation product with naphtalensulphonic acids, natural tannins, syntans or miscelate with lignin sulphonic extract. An example of formula structure for dicyandiamide-formaldehyde- naphtalensulphonic acids resin is reported:



As pointed out in the figure, the structure of resin present nitrile groups that can give bounds to the carboxylic groups of collagen proteins.

### Ecological aspects

It is very important to analyze the environmental impact of those products. Inorganic salts in the waste-water are a problem of these products since generally compounds like sodium sulphate or ammonium sulphate are produced during the synthesis to make water-soluble the aromatics (sulphonation reaction).



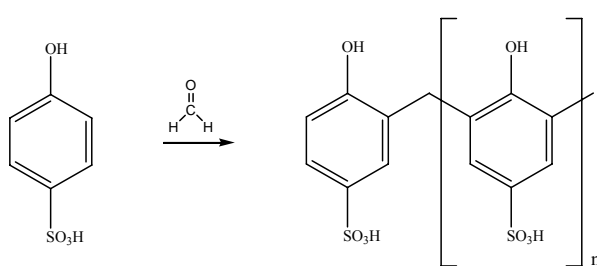
Another problem is the free-formaldehyde in the products and subsequently in the leather. In the following table the possibility of formaldehyde emission from various leather chemicals is listed.

CHEMICAL	FREE FORMALDEYDE	
	EXPECTED CONTENT	POSSIBLE ORIGIN
Formaldehyde for tanning and cross-linking	High	Direct
Some polyacrylates, e.g. preservatives	Traces of free formaldehyde	composition residue
Resin type tannins		reversible bound formaldehyde, hydrolysable
Syantn type tannins		irreversible bound formaldehyde, condensation residue
Fatliquors, dyestuffs, vegetable polyacrylates, PU, formiate, acetate, self-basifying chrome	Formaldehyde-free organics	decomposition can lead to traces of formaldehyde

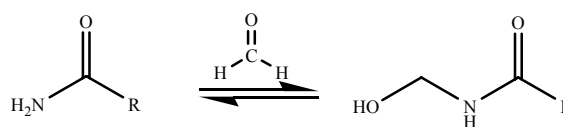
CHEMICAL	FREE FORMALDEYDE	
	EXPECTED CONTENT	POSSIBLE ORIGIN
reduced by molasses		
NaCl, Na <sub>2</sub> SO <sub>4</sub> , NaOH, basic chrome sulphate, etc	Formaldehyde-free inorganics	No carbon No formaldehyde

Due to its properties as preservative, formaldehyde has been extensively used in the past to stabilize organic products against microbiological decomposition, and not all of suppliers have updated their compositions to a less dangerous biocide yet. Resins are one product class which contains trace amounts of formaldehyde in the product or may be decomposed to liberate it, due to their chemical structure.

During the synthesis of syntans the formaldehyde is irreversibly bound and in this case free formaldehyde can be due to not optimal manufacturing process. Instead the resins could contain relevant amounts of formaldehyde because it is bound by an equilibrium reaction and small amount can remain free. Furthermore, the new chemical species, such as methylol groups, can react like formaldehyde and, under unfavourable conditions, can easily leach it.



**Syntans, irreversible bound**



**Resins, reversible bound**

### *Experimental*

15 different acrylic copolymers produced by different companies were studied. The chemicals and their descriptions, based on technical and safety data sheets, are listed in table 1.

Furthermore, 8 not-acrylic products, listed in table 2 with pointing of the declared main polymer/copolymer type, have been tested.



**Table 1. Summary of examined acrylic polymers**

Supplier	Code	Description
A	1	Acrylic acid-acrylamide copolymer in water solution
	2	Polyacrylic in water solution
	4	Acrylic esters copolymer in emulsion
B	6	Water soluble acrylic polymer
	7	Acrylic acid-vinyl acetate copolymer in water solution
C	10	Acrylic copolymer in water solution
	11	Acrylic polymer
D	12	Polyacrylate in water solution
E	13	Acrylic polymer in water solution
F	14	Polyacrylic resin
G	15	Polyacrylate, ammonium salt
H	16	Acrylic resin
I	18	Acrylic copolymer
	19	Polymer derived from acrylic acid

**Table 2. description of resins investigated**

Supplier	code	Description	Main Polymer/Copolymer type
B	9	Melamine-urea-formaldehyde polymer/sulphated polymer	MEL
L	21	urea-formaldehyde polymer/ phenol-formaldehyde polymer	UPF
L	22	Melamine-urea-formaldehyde polymer	MEL
I	24	Amphoteric Melamine resins in aqueous solution	MEL
A	5	Polymer on base of dicyandiamide, formaldehyde and sodium bisulfite	DCY
D	27	Product of condensation methylene bond of arylsulphonic acid and dicyandiamide	DCY
D	28	Product of condensation methylene bond of dicyandiamide	DCY
H	29	Dicyandiamide resin	DCY

MEL = melamine; UPF = urea-phenol-formaldehyde; DCY = dicyandiamide

On these products, we have carried out the following analytical determinations:

- Water content by Marcusson procedure
- Moisture and volatile matter at 102°C
- Total ashes at 550 °C

- Spectrophotometric determination of free formaldehyde, only on condensate products
- IR spectroscopy

From these determinations we have calculated:

- the volatile matter content, as the difference of values of moisture and volatile matter at 102°C and water content;
- the dry residue, correlated to active matter, as complement to 100 of value of moisture and volatile matter at 102°C;
- the organic substances, as the difference between dry residue and total ashes at 550°C.

## ***Results and discussion***

### **Chemical analysis**

#### ***Acrylic Polymers***

The results of chemical determinations performed on acrylic polymers are listed in table 3.

**Table 3. Chemical analysis of acrylic polymers**

<b>Code</b>	<b>A</b>	<b>B</b>	<b>C=A-B</b>	<b>D=100-A</b>	<b>E</b>	<b>F=D-E</b>
	<b>Moisture and volatile matter at 102°C</b>	<b>Water</b>	<b>Volatile matter</b>	<b>Dry residue</b>	<b>Total ashes at 550°C</b>	<b>Organic substances</b>
<b>1</b>	70,5%	65,3%	5,2%	29,5%	11,4%	18,1%
<b>2</b>	60,4%	57,7%	2,7%	39,6%	11%	28,6%
<b>4</b>	68,3%	67,4%	0,9%	31,7%	0,1%	31,6%
<b>6</b>	70,1%	68,8%	1,3%	29,9%	14,8%	15,1%
<b>7</b>	74,7%	74,0%	0,7%	25,3%	7,6%	17,7%
<b>10</b>	60%	50,5%	9,5%	40,0%	0,1%	39,9%
<b>11</b>	61,7%	56,7%	5,0%	38,3%	16,2%	22,1%
<b>12</b>	59,2%	57,4%	1,8%	40,8%	11,7%	29,1%
<b>13</b>	59,8%	59,8%	0,0%	40,2%	19,2%	21,0%
<b>14</b>	68,9%	68,9%	0,0%	31,1%	0,1%	31,0%
<b>15</b>	74,9%	72,0%	2,9%	25,1%	12,6%	12,5%

**Table 3. Chemical analysis of acrylic polymers**

	<b>A</b>	<b>B</b>	<b>C=A-B</b>	<b>D=100-A</b>	<b>E</b>	<b>F=D-E</b>
<b>Code</b>	<b>Moisture and volatile matter at 102°C</b>	<b>Water</b>	<b>Volatile matter</b>	<b>Dry residue</b>	<b>Total ashes at 550°C</b>	<b>Organic substances</b>
<b>16</b>	75,6%	67,7%	7,9%	24,4%	12,5%	11,9%
<b>18</b>	56,9%	44,2%	12,7%	43,1%	14,0%	29,1%
<b>19</b>	75,3%	70,4%	4,9%	24,7%	11,5%	13,2%
<b>20</b>	59,7%	43,2%	16,5%	40,3%	15,5%	24,8%
<b>Mean value</b>	<b>66,4</b>	<b>61,6</b>	<b>4,8</b>	<b>33,6</b>	<b>10,6</b>	<b>23,0</b>

The dry residue have a mean value of 33,6%, and is generally in agreement with the value reported by the suppliers in the technical data sheets.

In most of cases volatile matter at 102°C is mainly due to water (66,5%) but in the samples 20, 18, 10 volatile organic matter is respectively 16,5%, 12,7% and 9,5%.

According to mean values, the 60% of dry residue is constituted of organic substance while the remaining 40% is inorganic or mineral substance; only in three samples (4, 10 and 14) inorganic substances are negligible (ashes at 550°C =0,1%) and dry residue is due to only acrylic polymer.

### **Resins**

The analytical results of chemical determinations performed on resins are shown in table 4.

**Table 4. Chemical analysis of investigated resins**

<b>Code</b>	<b>Type</b>	<b>Moisture and volatile matter at 102°C</b>	<b>Dry residue</b>	<b>Total ashes at 550°C</b>	<b>Organic substances</b>
5	DCY	2,8	97,2	39,0	58,2
27	DCY	4,0	96,0	20,6	75,4
28	DCY	6,8	93,2	41,9	51,3
29	DCY	6,7	93,3	46,0	47,3
<b>Mean value DCY</b>		<b>5,1</b>	<b>94,9</b>	<b>36,9</b>	<b>58,0</b>
9	MEL	5,7	94,3	30,2	64,1
22	MEL	4,1	95,9	29,9	66,0
24	MEL	59,6	40,4	11,5	28,9
<b>Mean value MEL</b>		<b>23,1</b>	<b>76,9</b>	<b>23,9</b>	<b>53,0</b>
21	UPF	3,5	96,5	41,9	54,6

With exception of product 24, all the resins are in powder form and present a low moisture content, resulting in an high mean value of dry residue (approximately 95%).

Also in this case, all the products show not negligible amounts of mineral substances, and in particular, dicyandiamide resins present a mean value equal to 36,9%, while the content in the product 21, reported as an urea-phenol-formaldehyde resin, is even higher (41,9%).

Since the same results are obtained with acrylic polymers, further analysis are in progress to reach more deep knowledge on the nature and origin of mineral matter.

In order to evaluate the environmental impact, analyses of free formaldehyde content have been carried out by spectrophotometric method with acetylacetone. The obtained results are listed in Table 5.

**Table 5. Free formaldehyde analysis on investigated resin**

Code	Type	Formaldehyde	
		<i>mg/Kg</i>	<i>mg/Kg on dry weight</i>
5	DCY	8.370	8.610
27	DCY	Absent	Absent
28	DCY	4.780	5.130
29	DCY	Absent	Absent
9	MEL	12.460	13.210
22	MEL	16.900	17.620
24	MEL	4.950	12.250
21	UPF	1.290	1.340

In the products 27 and 29, both of dicyandiamidic type, the free formaldehyde is absent, but all the other resins show an high content and in particularly resins 9, 22, 24, all of melaminic type, exceed the value of 10.000 ppm on dry weight. These values can be explained according to the considerations reported in the “Ecological aspects” section.

## **IR Analysis**

### ***Acrylic Polymers***

The retanning agents were analysed by IR (FT-IR in ATR) in order to reach the chemical identification of active matter of products, in terms of functional groups that can characterize the copolymers or their constituent monomers.

The spectra show that there are different types of copolymer. In particular the spectra (see Fig. 1 and 2) of products 12, 13, 2, 20, 11 are similar and characteristic peaks are present to show the structure of a ternary copolymer. In fact:

- the peak at  $2243\text{ cm}^{-1}$  due to  $\text{-C}\equiv\text{N}$  stretching vibration prove that the structure includes nitriles, probably derived from residues of acrylonitrile
- the peak at  $1667\text{ cm}^{-1}$  can be assigned to  $\text{-C=O}$  stretching vibration of amide (amide I band), probably due to acrylamide and
- the peaks at  $1553$  and  $1402\text{ cm}^{-1}$ , assigned respectively to symmetric and asymmetric stretching vibration of carboxylate group, can be related to presence of acrylates.

A more deep analysis of spectra points out that the sample 2 show a different ratio between the peaks, that can be attributed to a different ratio between monomer. In particular, as you can see in Fig. 2, that presents a comparison with two spectra of acrilamide-acrylate copolymers with known content of acrylate residue, the presence of a peak at  $1614\text{ cm}^{-1}$ , known as amide II band, is an evidence of an higher percentage of acrylamide monomer respect to acrylate.

The spectra IR of samples 18, 15, 19, 1, 6, 16 are similar to spectra in fig 1. However the absence of peak at  $2240\text{ cm}^{-1}$  suggests that in these polymer there are not monomers of acrylonitrile but probably they are copolymers of acrylamide and salts of acrylic acid.

The spectra of samples 10, 7, 4 (see Fig. 3) are indicative of the peculiar characteristics of these products.

The sample 10 presents carboxylic acid residues with a peak at  $1692\text{ cm}^{-1}$  attributed at  $\text{C=O}$  of carboxylic acids and a strong hydrogen bonding resulting from the distortion of  $\text{-OH}$  stretching vibrations in range  $2700\text{-}2500\text{ cm}^{-1}$ .

The IR spectra of sample 7, confirms the presence of vinylacetate monomer declared in the technical data sheet. In fact:

- the peaks at  $1720\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  can be attribute to stretching of the  $\text{-C=O}$  and  $\text{-C-O}$  groups in acetate residues respectively, and
- the peak at  $2938\text{ cm}^{-1}$  is due to stretching of carbon-hydrogen link in the methylic group of acetate, which asymmetric and symmetric bending are visible at  $1447\text{ cm}^{-1}$  and  $1377\text{ cm}^{-1}$ .

In the spectrum of sample 4, typical absorption peaks of the polyacrylate can be observed at  $1725\text{ cm}^{-1}$  ( $\text{C=O}$  stretching vibration) at  $1242$  and  $1155\text{ cm}^{-1}$  ( $\text{C-O-C}$  stretching).

### ***Resins***

Examination of IR spectral data enables us to establish that all examined products are sulphitated, as the spectra show peaks at  $1180$  and  $1030\text{ cm}^{-1}$  due to sulphonic group ( $\text{-SO}_3\text{H}$ ). These evidence

could be related with the high mineral matter content resulting from chemical analysis, but confirmation are needed by further analytical investigations.

The figure 4 shows the spectra of melaminic resins 9, 22, 24, which are characteristic of MUF resins with the following peaks:

- at  $3333\text{ cm}^{-1}$  imputed to stretching hydroxy and amino groups;
- at  $1660\text{ cm}^{-1}$  due to stretching C=O of urea;
- at  $1555\text{ cm}^{-1}$  attributed to asymmetric stretch of side chain carbon-nitrogen groups;
- at  $813\text{ cm}^{-1}$  is due to ring-sextant-out-of-plane bending type of vibration in melamine.

Moreover the peak at  $1120\text{ cm}^{-1}$  can indicate the formation of ether linkages beside of methylene linkages.

The other resins have point out the presence of dicyandiamide monomer showing a peak at  $2170\text{ cm}^{-1}$ . In particular beside this peak, it is possible to identify characteristic signals in the ternary compound as dicyandiamide, formaldehyde and aryl sulphonic acid. In fig 5 the spectrum IR of sample 27 is shown. The peaks at  $1180$  and  $1030\text{ cm}^{-1}$  are respectively symmetric and asymmetric –  $\text{SO}_3\text{H}$ . The guanidinic double linkage carbon-nitrogen appears within the range  $1680\text{-}1650\text{ cm}^{-1}$ , however in this case the peaks are poorly resolved and overlap to the bands due to the aryllic aromatic ring.

## ***Conclusions***

The acrylic polymers and synthetic amine resins are classes of substances that are utilized widely in tanning process and particularly in retanning process.

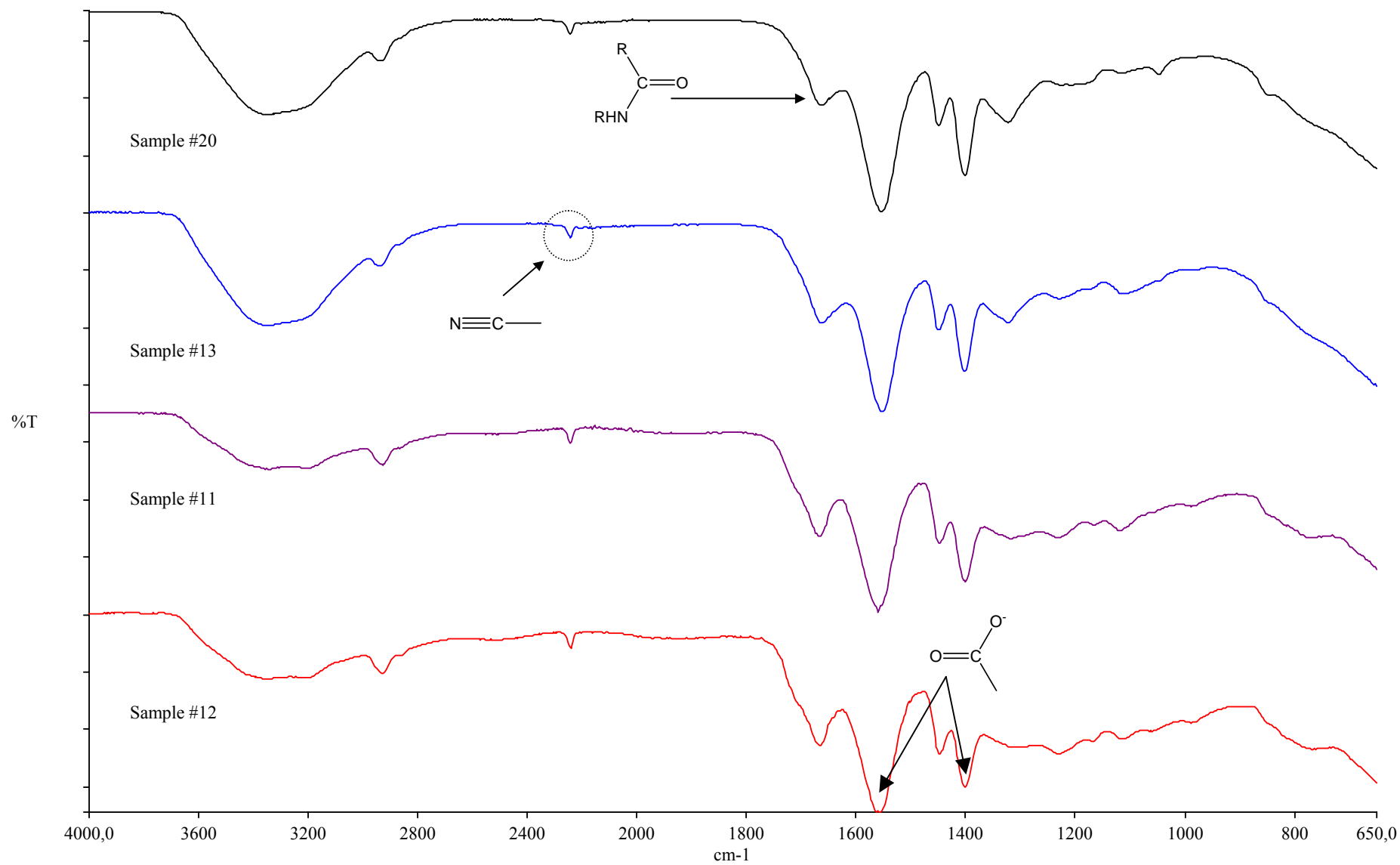
The characterization of these products has pointed out that in most of cases, beside organic substances, there is an considerable amount of inorganic or mineral matter. Then the active substance, declared in technical data sheets contains, not only polymers and their combinations but inorganic products too.

The IR analysis show that products, sold by different suppliers, present the same kind of active matter. In most of investigated acrylic copolymers, acrylonitrile groups are present as resulting of presence of characteristic peaks of triple bond carbon-nitrogen.

As to the resins, the IR spectra have allowed to identify, beside the peaks of main groups of copolymers, the characteristic peaks of sulphitated groups.

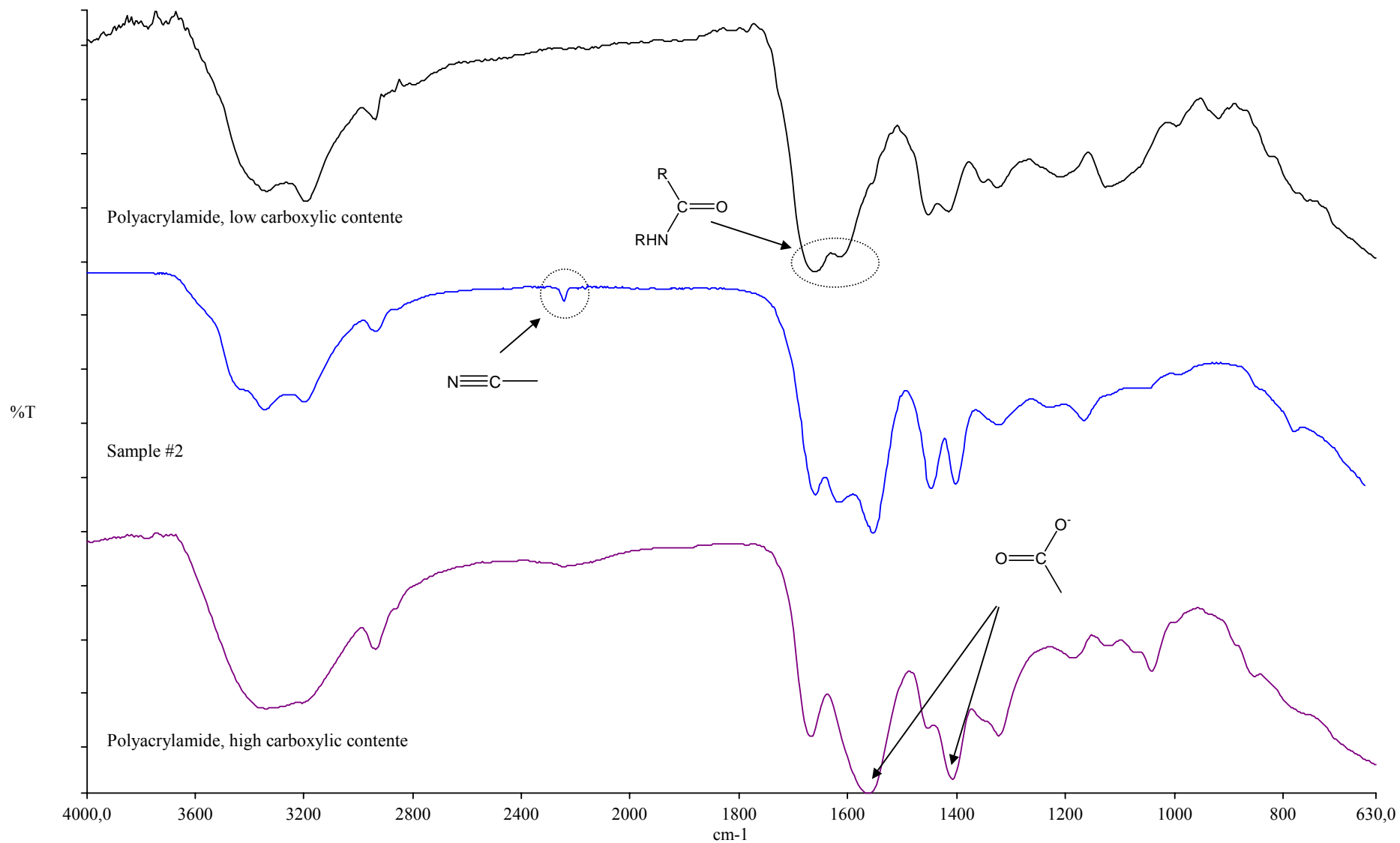
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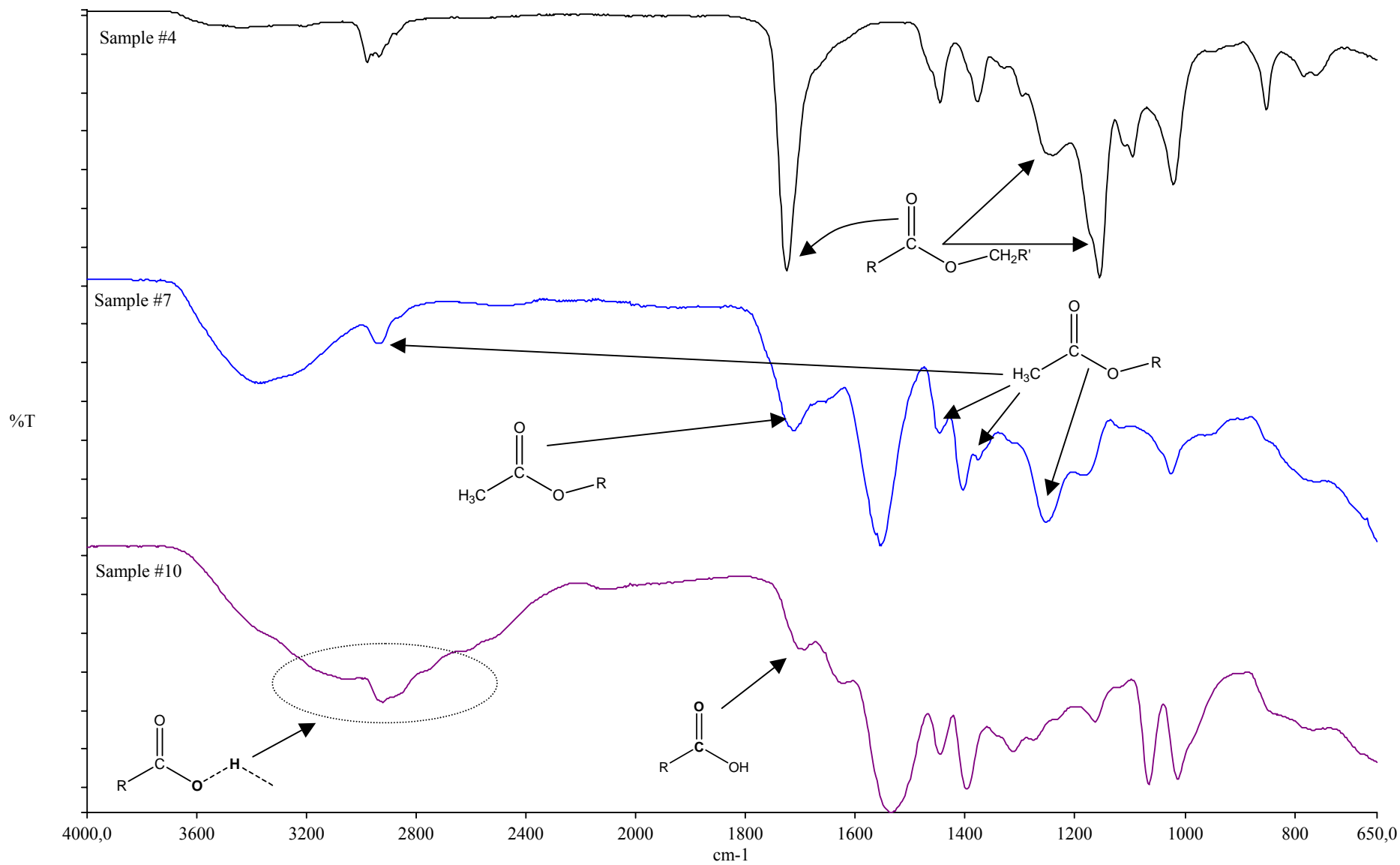


**Fig. 1. IR spectra of samples 12, 11, 13, 20**

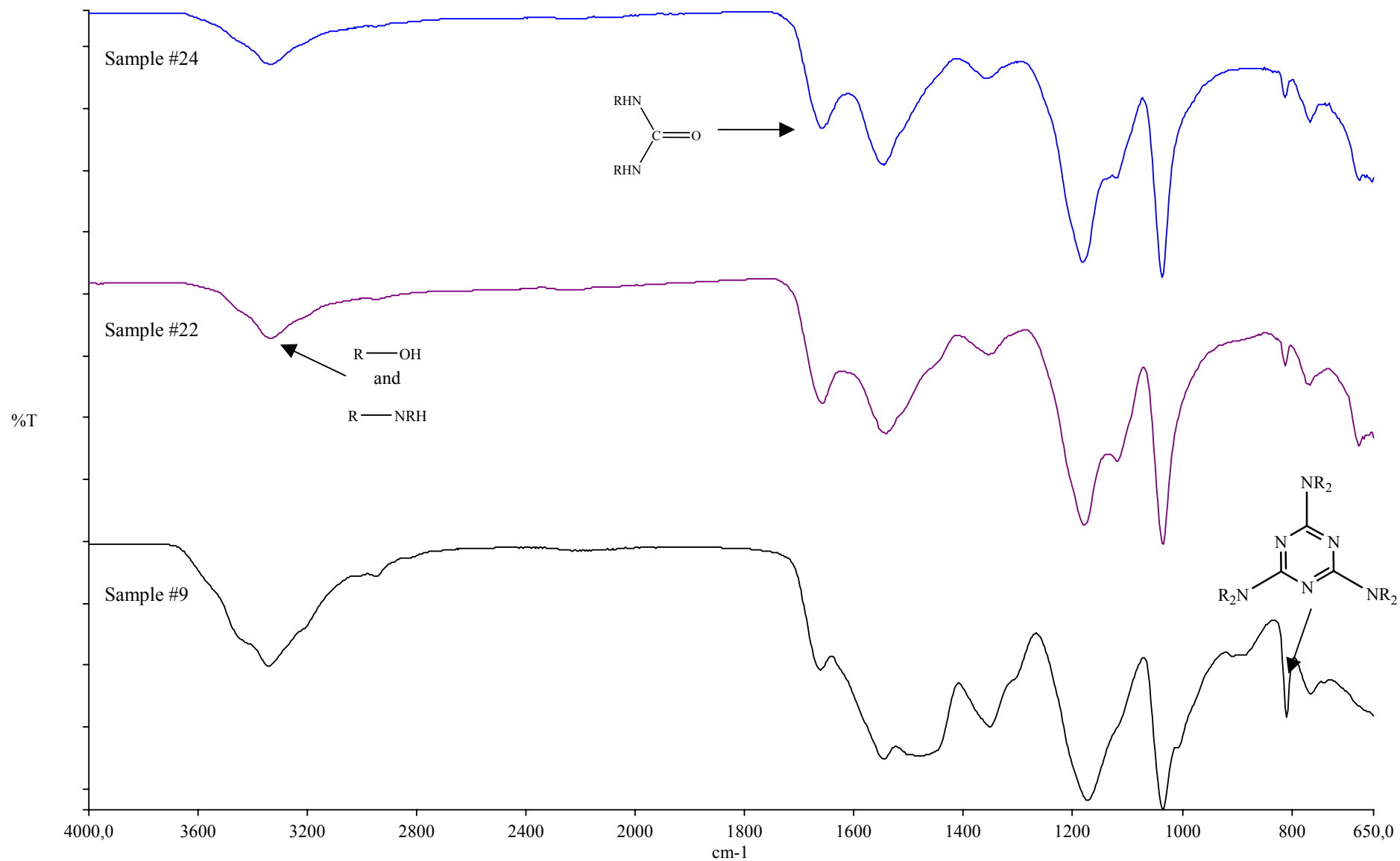




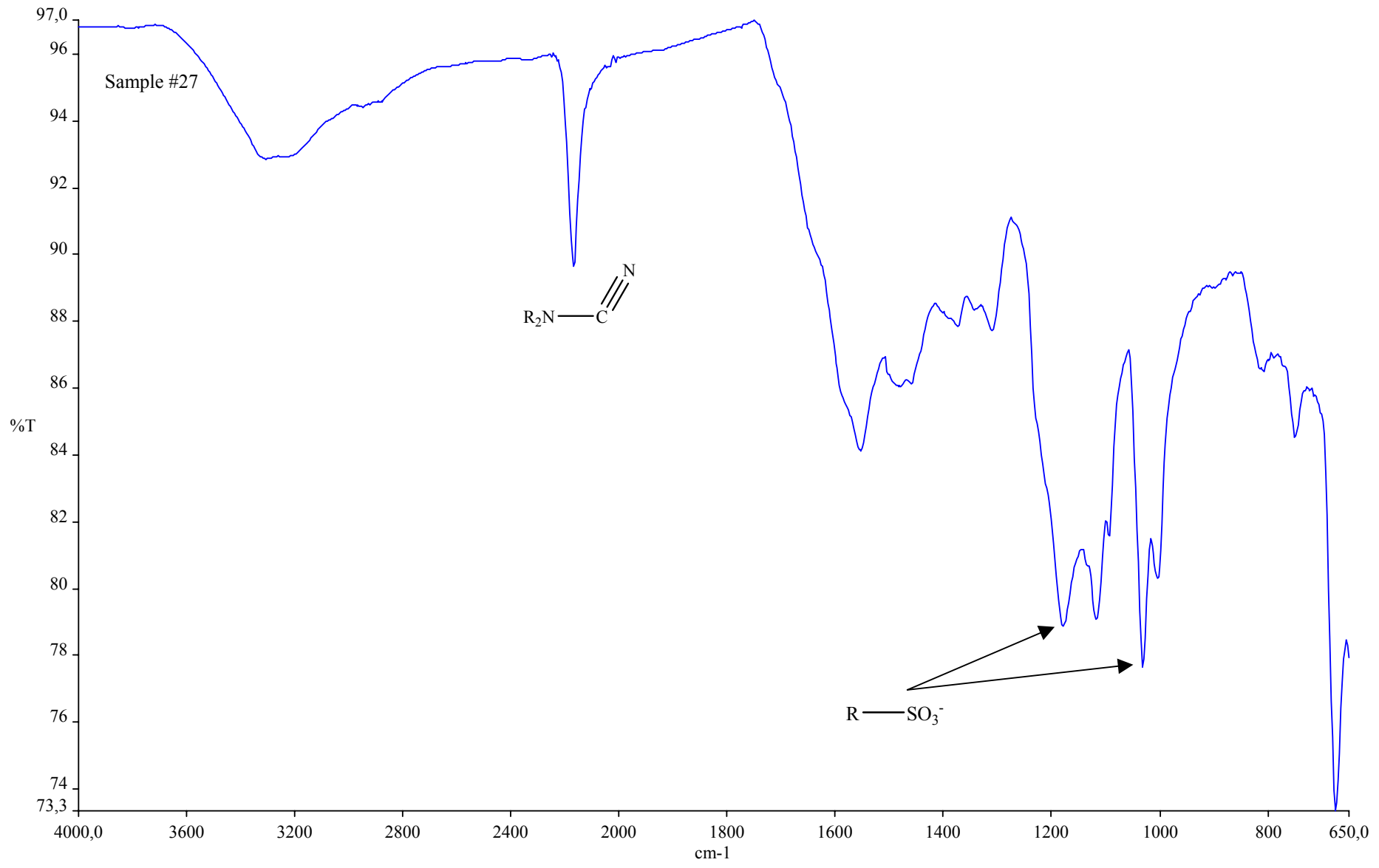
**Fig. 2.** IR spectra of sample 2 compared with two spectra of acrilamide-acrylate copolymers with known content of carboxylic residue



**Fig. 3. IR spectra of samples 10, 7 and 4**



**Fig. 4. IR spectra of melaminic resins - samples 9, 22 and 24**



**Fig. 5. IR spectra of dicyandiamydic resins – sample 27**