FEDERCHIMICA
AVISA
GRUPPO ADESIVI E SIGILLANTI

GUIDELINES
ADHESIVES FOR
FOOTWEAR AND LEATHER GOODS

April 2021

Responsible Care®
OUR COMMITMENT TO SUSTAINABILITY

GUIDELINES
ADHESIVES FOR
FOOTWEAR AND LEATHER GOODS

April 2021

AVISA is one of the 17 Sector Associations of Federchimica, the Italian Federation of the Chemical Industry, part of Confindustria and a member of CEFIC (European Chemical Industry Council).
AVISA represents companies producing adhesives and sealants, printing inks, paints and varnishes. The Association is entrusted with the exclusive task of representing and safeguarding the interests of its member companies, dealing with problems of specific interest to the sector, providing technical and economic assistance to its member companies and protecting its image.

TABLE OF CONTENTS

1. The Footwear and Leather Goods Adhesives Sector

The market of adhesives for footwear and leather goods in Italy amounts to 18,600 tonnes of products, with a turnover of approximately 73 million Euro*. 84% of the quantities are solvent-based adhesives, as shown in the table below, 10% are adhesives in water dispersion and the remaining 6% belong to the category of hot melt adhesives. Recently, there has been a process of converting some production lines to water-based technology, which has a lower environmental impact.

Italian Market 2018 *(Tons)*	Footwear		
	Footwear manufacturers	Total	2018/2017
ADESIVI		**18.600**	**-1%**
Natural Adhesives			
Water-Based Adhesives			
Water Dispersion Adhesives		**1.800**	**0%**
- Acrylics and acrylic copolymers		**50**	
- EVA Copolymers		**50**	
- Vinyl homopolymers (Polyvinyl acetate)		**70**	
- Vinyl copolymers		**60**	
- Polyurethanes		**730**	
- Polychloroprenics		**380**	
- Natural lactics		**320**	
- Styrene-butadiene (SBR) and carboxylate (CSBR)		**140**	
Solvent based Adhesives		**15.630**	**-1%**
- Polychloroprenics		**7.550**	
- Polyvinylether		**-**	
- Polyurethanes		**7.700**	
- Styrene-butadiene-styrene rubbers (SBSR)		**20**	
- Natural rubbers		**160**	
- Others in solvent		**200**	
Hot melt		**1.170**	**0%**
- Polyesters		**500**	
- Polyamides		**480**	
- EVA Copolymers		**90**	
- Polyurethanes		**60**	
- Polychloroprenics		**-**	
- Styrene rubbers (SBSR,SISR,SEBSR)		**40**	

Source: Research 'The adhesives and sealants market in Italy - year 2018'. Avisa Federchimica adhesives and sealants Group

Back to TOC

2. Purpose of the Guidelines

The footwear and leather goods adhesives manufacturers, members of AVISA-Federchimica, have drawn up these Guidelines with the aim of making their experience available to market players.

This document, based on their knowledge of national and EU standards, as well as of the products and raw materials of the chemical supply chain, aims to meet many and different requests received by member companies as:

a. a tool to help them standardise their eco-sustainability and worker safety standards to thresholds congruent with current industrial purification limits;
b. a meeting point between raw material producers and end users to contribute, where possible, to raising environmental and health protections;
c. contribution of the industry to the technical-scientific knowledge of adhesives and their correct use.

Back to TOC

3. Scope of application

This document relates to adhesives, cleaners, thinners and primers (see section 4 for details) used for the industrial or professional manufacture/repair/preparation of footwear and leather goods (see section 5 for an overview of materials concerning these sectors). In detail, the products considered here can be used directly or as additives/coadjuvants/hardeners for operations of:

- Bottom bonding (inserts, treads)
- Upper assembly
- Direct injection onto uppers
- Various lining and splicing operations for upper construction
- Wrapping of heels and wedges
- Production of insoles
- Lining
- Decoration and customisation
- Preparation/priming, UV marking and cleaning of materials

In the field of leather goods, the above-mentioned adhesives are used in the production of bags, wallets, belts for bonding various leathers and fabrics, both natural and synthetic.

Back to TOC

4. Types of adhesives

Bonding, as we have outlined in section 3, is an activity involving different types of chemicals. To simplify, we could divide them into six main categories:

A. Polyurethane-based adhesives:
These are generally solutions (in organic solvent) or colloidal dispersions (in water) of one or more polyurethane polymers (or related molecules) and, possibly, additives and stabilisers. The characteristics that determine the field of application and mode of use are related to:
- to the length/type of the polymer chain and its degree of crystallization, properties that correlate directly with the softening temperature (reactivation) and rheology (viscosity);
- to the polymer's degradability or, in other words, to its reactivity with water, light and heat or other interfering substances such as oils, greases and release agents;
- or to other properties, conferred by special additives, such as electrical conductivity, colour, wettability or heat resistance.

Visually they appear as homogeneous mixtures: transparent or opalescent with solid content typically less than 20% by weight (if solutions in organic solvent); white or opalescent with solid content typically around 50% by weight (if in aqueous dispersion).
The adhesive can be applied by brush, roller or spray. The film forms once the volatile part of the solution/dispersion has evaporated. It appears completely transparent and, with a few exceptions, non-sticky. Adhesion develops by softening the polyurethane layer deposited on the surfaces to be bonded and coupling them with adequate pressure. The two separate films come into contact with each other and merge to form a single one.

B. Neoprene-based adhesives:
These are solutions (in organic solvent) or colloidal dispersions (in water) of polychloroprene (one or more grades), resins (various types) and, possibly, additives and stabilisers.
The characteristics that determine the field of application and mode of use of these adhesives are related:
- to the length/type of the polymer chain, properties that correlate directly with open time and rheology (viscosity);
- to other properties, conferred by special additives, such as electrical conductivity, colour, wettability, temperature resistance.

Visually they appear as homogeneous mixtures: yellow (ochre to orange-red) with dryness typically around 20% by weight (if solutions in organic solvent); white with dryness typically around 50% by weight (if in aqueous dispersion).
The adhesive can be applied by brush, roller or spray. The film forms once the volatile part of the solution/dispersion has evaporated. It appears sticky, yellow/ochre (solvent-based adhesive) or transparent (water-based adhesive). Adhesion develops, within the limits of the open time (i.e. before the film loses its stickiness), by coupling the materials with light pressure at temperatures close to room temperature. The two separate films come into contact with each other and fuse to form one.

Back to TOC

C. Other adhesives

These are solutions (in organic solvents) or dispersions (in water) based on

- polyvinyl acetate (or related molecules/copolymers). We are talking here about the large field of vinyl adhesives
- natural rubber, synthetic rubber or rubber latex
- cyanoacrylates
- ethylene vinyl acetate (EVA)

D. Primers

Primers are bonding aids: they make one or more of the adhesives mentioned in the previous points compatible with a specific substrate.

There are essentially three principles of action of primers:

- by penetration into the substrate:
  the primer, in this case, has a similar chemical composition and a dryness equal to or lower than the corresponding adhesive, but a lower viscosity. This characteristic allows the product to penetrate porous substrates and create a polymer layer chemically similar to the adhesive that will be applied over it;

- by chemical-physical affinity:
  the primer, despite having a different composition from both the support and the adhesive, having an affinity with both, is able to create a chemical bridge between the two layers allowing the bonding;

- by chemical reaction:
  these are solutions of resins or salts (organic or inorganic) which, reacting with one or more components of the support to be bonded, promote the subsequent anchorage of the polyurethane, neoprene or vinyl adhesive.

E. Activators

These are organic solvent solutions or water dispersions of isocyanates. This category of molecules is able to interact with the polymers of adhesives by promoting the formation of additional bonds between the chains. This reactivity enables the 'cross-linking' of adhesives: that is, it promotes resistance to hydrolytic degradation and increases the temperature at which the polymer softens. The latter characteristic gives greater bonding strength under conditions of thermal stress during use.
Some isocyanates, locked in microspheres that can only break upon reactivation, may be found directly within the water-based adhesive.
In other applications, they are used as a second component in primer systems for the chemical treatment of certain materials.

F. Cleaners

These are mixtures of organic solvents or solutions of surfactants and other additives in water used for cleaning supports from interfering bonding agents (release oils, anti-adhesive or coloured finishes, dust or other residues), for diluting adhesive mixtures or cleaning the tools/machines used for applying the products.

Back to TOC

5. Types of materials

In the footwear and leather goods sector, as in all the main production areas, progress has introduced over time, in particular in the last 20 years, various innovations in the field of materials, their preparation and production. This innovation has marked research in the field of adhesives, contributing to the multiplication of bonding chemicals as summarised in the previous section. Today, the most widely used materials can be identified among the following:

- Traditional leathers, greased or with a water-repellent finish, bycast;
- Synthetic leathers;
- Synthetic fabrics (polyester, nylon etc.) or natural fabrics (wool, cotton, hemp etc.);
- Thermoplastic rubbers (SBS, SBR), cautchu, vulcanised rubber, thunit;
- Expanded and thermoplastic polyurethane;
- Microcellular and thermoformed EVA;
- cellulosic materials, cardboard and fibreboard;
- Glass;
- Leather;
- Aluminium and steel;
- Carbon fibre;
- Wood;
- Other plastics from synthesis such as: PVC, Polyolefins (PP,PE etc.), ABS, Hypalon, Neoprene, Nylon, Polystyrene, Polycarbonate, Polymethylmethacrylate, Cellulose, Polyester, Polyether;
- Composite materials prepared by cutting different polymers such as TPU-rubber and others.

Back to TOC

6. MRSL List (analyte, CAS number, concentration limit and method of analysis)

6.1 List and methods

CLASS	Analyte	CAS Number	TYPE OF ADHESIVE		LIMIT concentration limit proposed [ppm]	ANALYTICAL METHODS	LOD	LOQ	Instrument
			SOLVENT BASED	WATER BASED					
ALKIL PHENOLS	4NP	84852-15-3	x		250	ISO 18857-1	48,00	145,00	HPLC-fluorescence
	4-ter-OP	140-66-9	x		250	ISO 18857-1	49,00	147,00	HPLC-fluorescence
	4NPEO	68412-54-4	x	x	500	UNI EN ISO 18254-1		50,00	
	OPEO	9002-93-1	x	x	500	UNI EN ISO 18254-1		50,00	
POLYCHLORINATED BIPHENOLS	Penta clorophenol	87-86-5	x	x	100	UNI EN ISO 17070		0,10	
	tetrachlorophenol	25167-83-3	x	x		UNI EN ISO 17070		0,10	
	2,3,4,5-tetrachlorofenol	4901-51-3	x	x		UNI EN ISO 17070		0,10	
	2,3,5,6-tetrachlorophenol	935-95-5	x	x		UNI EN ISO 17070		0,10	
	2,3,4,6-tetrachlorophenol	58-90-2	x	x		UNI EN ISO 17070		0,10	
	2,3,4-trichlorophenol	15950-66-0	x	x		UNI EN ISO 17070		0,10	
	2,3,5-trichlorophenol	933-78-8	x	x		UNI EN ISO 17070		0,10	
	2,3,6-trichlorophenol	933-75-5	x	x		UNI EN ISO 17070		0,10	
	2,4,5-trichlorophenol	95-95-4	x	x		UNI EN ISO 17070		0,10	
	2,4,6-trichlorophenol	88-06-2	x	x		UNI EN ISO 17070		0,10	
	3,4,5-trichlorophenol	609-19-8	x	x		UNI EN ISO 17070		0,10	
	orthophenylphenol	90-43-7	x	x	1000	UNI EN ISO 11890-2		100,00	
OTHER SUBSTANCE	Formaldehyde	50-00-0	x	x	75	UNI EN ISO 14184-1		16,00	
METALS	As	7440-38-2	x	x	50	ISO 17072-2:2019	0,91	2,72	ICP-MS
	Cd	7440-43-9	x	x	20	ISO 17072-2:2019	0,44	1,33	ICP-MS
	Cr	7440-47-3	x	x	100	ISO 17072-2:2019	0,83	2,50	ICP-MS
	Cr (VI)	18540-29-9	x	x	10	UNI EN ISO 17075-1:2017	1,60	4,80	spectrophotometer
	Pb	7439-92-1	x	x	100	ISO 17072-2:2019	1,10	3,31	ICP-MS
	Hg	7439-97-6	x	x	10	ISO 17072-2:2019	1,05	3,16	ICP-MS
	Ni	7440-02-0	x	x	100	ISO 17072-2:2019	0,64	1,91	ICP-MS
	Cu	7440-50-8	x	x	100	ISO 17072-2:2019	2,65	7,95	ICP-MS
	Sb	7440-36-0	x	x	100	ISO 17072-2:2019	1,49	4,48	ICP-MS
	Co	7440-48-4	x	x	100	ISO 17072-2:2019	2,94	8,83	ICP-MS
ORGANOTIN	DBT	1002-53-5	x	x	20	ISO/TS 16179	0,10	0,30	GC/MS
	TCyHT	6056-50-4	x	x	1	ISO/TS 16179	0,10	0,30	GC/MS
	TPT	2279-76-7	x	x	1	ISO/TS 16179	0,10	0,30	GC/MS
	TeBT	1461-25-2	x	x	1	ISO/TS 16179	0,10	0,30	GC/MS
	TeOT		x	x	1	ISO/TS 16179	0,10	0,30	GC/MS
	TMT	1066-45-1	x	x	5	ISO/TS 16179	0,10	0,30	GC/MS
	DMT	753-73-1	x	x	5	ISO/TS 16179	0,10	0,30	GC/MS
	MPhT		x	x	5	ISO/TS 16179	0,10	0,30	GC/MS
HYDROCARBONS	Acenaphthene	83-32-9	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
POLYCYCLES	Acenaphthylene	208-96-8	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
AROMATIC	Fluorene	86-73-7	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Phenanthrene	85-01-8	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Fluoranthene	206-44-0	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Indenol(1,2,3-c,d)pyrene	193-39-5	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Benzo[ghi]perylene	191-24-2	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Anthracene	120-12-7	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Pyrene	129-00-0	x		100	ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Naphthalene	91-20-3	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Benzo(a)anthracene	56-55-3	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Benzo(b)fluoranthene	205-99-2	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Benzo(e)pyrene	192-97-2	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Benzo(j)fluoranthene	205-82-3	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Benzo(k)fluoranthene	207-08-9	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Chrysene	218-01-9	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Dibenzo(a,h)anthracene	53-70-3	x			ISO/TS 16190	0,003	0,009	HPLC-fluorescence
	Benzo(a)pyrene	50-32-8	x		20	ISO/TS 16190	0,003	0,009	HPLC-fluorescence

Back to TOC

CLASS	Analyte	CAS Number	TYPE OF ADHESIVE		LIMIT concentration limit proposed [ppm]	ANALYTICAL METHODS	LOD	LOQ	Instrument
			SOLVENT BASED	WATER BASED					
PFC	PFOA	335-67-1	x		5	UNI EN ISO 25101:2009	0,013	0,038	LC/MS
	PFOS	1763-23-1	x		5	UNI EN ISO 25101:2009	0,008	0,023	LC/MS
PHTHALATES	DINP	28553-12-0	x	x	somma 250	ISO/TS 16181	15,00	45,00	GC-ECD
	DNOP	117-84-0	x	x		ISO/TS 16181	15,00	45,00	GC-ECD
	DEHP	117-81-7	x	x		ISO/TS 16181	15,00	45,00	GC-ECD
	DIDP	26761-40-0	x	x		ISO/TS 16181	15,00	45,00	GC-ECD
	BBP	85-68-7	x	x		ISO/TS 16181	15,00	45,00	GC-ECD
	DBP	84-74-2	x	x		ISO/TS 16181	15,00	45,00	GC-ECD
	DIBP	84-69-5	x	x		ISO/TS 16181	15,00	45,00	GC-ECD
	DnHP (DHEXP)	84-75-3	x	x		ISO/TS 16181	15,00	45,00	GC-ECD
	DEP	84-66-2	x	x		ISO/TS 16181	15,00	45,00	GC-ECD
SOLVENTS	DMFa	68-12-2	x		500	EN ISO 167789:2016	0,50	1,50	GC/MS
	DMAC	127-19-5	x		1000	UNI EN ISO 11890-2		100,00	
	NMP	872-50-4	x	x	1000	UNI EN ISO 11890-2		100,00	
	2-ethoxyethanol	110-80-5		x	50	**	1,70	5,00	GC/MS
	2-Metoxypropylacetate	70657-70-4		x	50	**	1,70	5,00	GC/MS
	Ethyl 2-ethoxyacetate	111-15-9		x	50	**	1,70	5,00	GC/MS
	Bis(2-methoxyethyl)-ether	111-96-6		x	50	**	1,70	5,00	GC/MS
	2-Methoxyethanol	109-86-4		x	50	**	1,70	5,00	GC/MS
	EGDME	110-71-4		x	50	**	1,70	5,00	GC/MS
	2-Methoxyethylacetate	110-49-6		x	50	**	1,70	5,00	GC/MS
	TEGDME	112-49-2		x	50	**	1,70	5,00	GC/MS
	Dichloromethane	75-09-2	x		10	EN ISO 22155	0,50	1,50	GC/MS
	1,2 Dichloroethane	107-06-2	x		10	EN ISO 22155	0,50	1,50	GC/MS
	Tetrachloroethylene	127-18-4	x		10	EN ISO 22155	0,50	1,50	GC/MS
	Trichloroethylene	79-01-6	x		40	EN ISO 22155	0,50	1,50	GC/MS
	2-Chlorotoluene	95-49-8	x		somma 250	UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	3-Chlorotoluene	108-41-8	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	4-Clorotoluene	106-43-4	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	2,3-Dichlorotoluene	32768-54-0	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	2,4-Dichlorotoluene	95-73-8	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	2,5-Dichlorotoluene	19398-61-9	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	2,6-Dichlorotoluene	118-69-4	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	3,4-Dichlorotoluene	95-75-0	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	1,3-Dichlorobenzene	541-73-1	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	1,2,4,5-Tetrachlorobenzene	95-94-3	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	Pentachlorobenzene	608-93-5	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	Exachlorobenzene	118-74-1	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	1,2,4-Trichlorobenzene	120-82-1	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	1,2,3,5-Tetrachlorobenzene	634-90-2	x			UNI EN 17137:2019	(1.28)	(3.84)	GC/MS
	1,2-Dichlorobenzene	95-50-1	x		500	UNI EN 17137:2019	0,79	2,37	GC/MS
	Benzene	71-43-2	x	x	100	EN ISO 22155	0,50	1,50	GC/MS
	Ethylbenzene	100-41-4	x	x	500	EN ISO 22155	0,50	1,50	GC/MS
	Toluene	108-88-3	x	x	500	EN ISO 22155	0,50	1,50	GC/MS
	Xylene	1330-20-7	x	x	1500	EN ISO 22155	1,00	3,00	GC/MS
	o-Cresol	95-48-7	x		500	UNI EN ISO 11890-2		100,00	
	m-Cresol	95-48-7	x		500	UNI EN ISO 11890-2		100,00	
	p-Cresol	106-44-5	x		500	UNI EN ISO 11890-2		100,00	
** standard methods not available	Method for the determination of glycols (** in the table not associated to a specific ISO standard):								
	Procedure: dilute 1g of sample in 10mL of methanol, sonicate for 1h at 70°C then analyse in GC/MS (DB-WAX type column) headspace method.								

6.2 Substances seriously concerned

CLASS	Analyte	CAS Number	TYPE OF ADHESIVE		LIMIT concentration limit proposed [ppm]	ANALYTICAL METHODS	LOD	LOQ	Instrument
			SOLVENT BASED	WATER BASED					
Biocides	(CMIT)	26172-55-4							
	(MIT)	2682-20-4		x	100	No official standard			
	CMIT/MIT	55965-84-9		x	15	No official standard			
	(OIT)	26530-20-1		x	50	No official standard			
	(BIT)	2634-33-5		x	500	No official standard			

Back to TOC

7. Self-regulation

AVISA member companies undertake to comply with the following:

- *self-certification of standards*
  The ISO 9001-certified company, when asked, may issue a declaration of conformity for the requested products.

- *quality of analytical data*
  declarations are drawn up on the basis of accurate and reliable information in the company's possession or on the basis of analyses carried out by ISO IEC 17025 accredited laboratories, with frequency linked to significant variations in individual formulations/raw materials.

They also undertake to meet annually to review the guidelines, updating them to technological-scientific progress and, if necessary, adapting them to new national and EU legislation.

Back to TOC

We acknowledge for their participation in drafting the Guideline

Emiliano Bozzato - Industrie Chimiche Forestali S.p.A.
Fabio Chiozza - Vinavil S.p.A.
Giacomo Colombo - Roser Adesivi S.r.l.
Mario Fratoni - Frabo S.p.A.
Marco Marinelli - Frabo S.p.A
Marco Pigliafreddo - Industrie Chimiche Forestali S.p.A.
Antonio Sassi - Industrie Chimiche Forestali S.p.A.
Marcello Taglietti - Industrie Chimiche Forestali S.p.A.
Enrico Trevisani - F.lli Zucchini S.p.A.
Ezio Valente - H.B. Fuller Adhesives Italia S.p.A.

Contributors

Assunta Tralongo - Federchimica Avisa
Micaela Comber - Federchimica Avisa
Simone Galliena - Federchimica Avisa