HELPING YOU TO WORK MORE SAFELY

Improving occupational safety through a reduction in hazardous chemicals in LOCTITE® Instant Adhesives and Accelerators.

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INTRODUCTION

Over the past few years, Henkel has received increasing inquiries from users of our instant adhesive products regarding several ingredients that have come under greater regulatory scrutiny in select regions of the world. Of particular concern are ingredients identified as Carcinogenic, Mutagenic and Reproductive Toxins (CMRs), but there are other concerns also (e.g., health hazard pictograms on product labels). Many of the current commercially available instant adhesives contain two low-level ingredients classified as CMRs: Hydroquinone (HQ) and/or 2,2' and Methylenebis (4-methyl-6-*tert*-butylphenol) (MMBP). Similarly, current commercial grades of instant adhesive accelerators contain an ingredient which is a CMR: *N, N*-dimethyl-*p*-toluidine (DMPT).

In response to these regulatory concerns and the industrial market's demand for "safer" assembly solutions, several Henkel formulations have been upgraded with more globally acceptable raw materials. This innovation combines an upgraded formulation with the high quality and reliability for which the LOCTITE® brand is known. This has been achieved without compromising any of the key properties, including fixture times, bond strengths, material versatility and shelf-life. Several LOCTITE accelerators have also been included in this upgrade with no impact on product performance.

LOCTITE® INSTANT ADHESIVE SOLUTIONS AND HAZARDOUS CHEMICALS

As outlined, the market leading LOCTITE Instant Adhesive product range (and accompanying accelerators) were chosen by Henkel as a key product category for reduction in hazardous chemical ingredients. LOCTITE Instant Adhesives are high-performance products designed for the assembly of a wide range of substrates (including difficult-to-bond materials), that require uniform stress distribution and high tensile and/or shear strength. These products provide for the rapid bonding of various materials including metals, plastics and elastomers. Select formulas are also well-suited for bonding porous materials such as wood, paper, leather and fabric. There are a large number of products within the range combining rapid-curing liquid grades (e.g., LOCTITE 401™) and rapid-curing gel grades (e.g., LOCTITE 454™), which enable overhead and vertical applications. In recent years, novel two-part options have also been introduced (e.g., LOCTITE 3090™), combining rapid bonding and gap filling capabilities. Henkel also offers a range of accelerators (e.g., LOCTITE SF 7452/ 7455) which enhance cure speed.

The adhesive products selected for this hazardous ingredient reduction program include LOCTITE 401, LOCTITE 406,™ LOCTITE 495,™ LOCTITE 454, LOCTITE 3090 and LOCTITE 3092™ (Figure 1), and the accelerators included are LOCTITE 7455 and LOCTITE 7452 (Figure 2). Further work is intended in future years to expand this approach to other products within this category.

Significant customer and market studies were carried out to help define the types of ingredients that are of most concern to users. Every chemical manufactured and sold globally has a set of hazard statements and pictograms associated with it, based on the toxicological data available to provide guidance to the user on the risks associated with handling such chemicals. The rules for applying these hazard statements and pictograms are articulated through the Globally Harmonized System of Classification and Labelling of Chemicals (known as GHS). Such statements will appear on the product safety data sheet (SDS) and the associated hazard pictograms will appear on both the product safety data sheet and on the label of the product.
In general, Carcinogenic, Mutagenic and Reproductive Toxins (known as CMRs) were identified as the main

Figure 1. Instant adhesive products identified for reduction in hazardous ingredients.

Figure 2. Instant adhesive accelerators identified for reduction in hazardous ingredients.

hazards of concern. The hazard statements associated with such materials are shown in Table 1. In addition to the focus on specific CMR ingredients, this upgrade also focused on reducing any ingredients that may impart toxicity to aquatic organisms or result in an "Exploding Man" pictogram.

As mentioned, a review was carried out on the products selected for this program to identify the most hazardous components. The materials listed in Table 2 were highlighted as the targets for reduction.

The hazard statements of most concern for noted ingredients are shown in Table 3. The full list of statements associated with the material are also detailed in Appendix 1.

In the next sections, the technological advancements taken in the adhesive (Section 3), and accelerator and primer (Section 4) formulations will be explored in greater detail.

TABLE 1. Hazard Statements Associated with CMRs.

CARCINOGENIC	MUTAGENIC	REPRODUCTIVE
H350 May cause cancer.	**H340** May cause genetic defects.	**H360** May damage fertility or the unborn child.
H351 Suspected of causing cancer.	**H341** Suspected of causing genetic defects.	**H361** Suspected of damaging fertility or the unborn child.
		H362 May cause harm to breastfed children.

TABLE 2. Target Ingredients for Reduction or Elimination.

ABBREVIATION	CHEMICAL NAME	CAS NUMBER
HQ	Hydroquinone	123-31-9
MMBP	Bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl) methane	119-47-1
DMPT	*N, N*-dimethyl-*p*-toluidine	99-97-8

TABLE 3. Target Ingredients and Current Hazard Statements of Concern.

ABBREVIATION	HAZARD STATEMENTS
HQ	**H341** Suspected of causing genetic defects. **H351** Suspected of causing cancer.
MMBP	**H361** Suspected of damaging fertility or the unborn child.
DMPT	**H350** May cause cancer.

LOCTITE® INSTANT ADHESIVES

Hydroquinone (HQ) and 2,2'-Methylenebis(4-methyl-6-*tert*-butylphenol) (MMBP) are examples of free-radical stabilizers. They are essential additives for any instant adhesive formulation, with their primary purpose being to actively scavenge for free radicals that could trigger polymerization of the cyanoacrylate monomer. In other words, they ensure that the adhesive remains liquid in the bottle for the duration of its shelf-life. LOCTITE Instant Adhesives contain these chemicals in only very low amounts and the finished products are not classified as CMRs.

An extensive program was undertaken by the Henkel R&D team to identify and validate alternative free-radical stabilizers which are not classified as CMRs. The result is a novel free-radical stabilizer package which has allowed Henkel to remove HQ from the formulations of LOCTITE 401,™ LOCTITE 406™ and LOCTITE 495™—and HQ and MMBP from LOCTITE 454,™ LOCTITE 3090™ and LOCTITE 3092.™ These new ingredients do not need to be highlighted as hazard components on the product SDS, due to their low levels and excellent health and safety characteristics. Table 4 shows the current levels versus the new levels for the ingredients of concern, with the upgraded levels serving as a new specification limit to ensure

TABLE 4. Current vs. Upgraded Levels of CMR Ingredients per Henkel Product.

HENKEL PRODUCT	CURRENT PRODUCT LEVEL	UPGRADED PRODUCT LEVEL
LOCTITE 401	> 800 ppm HQ	< 50 ppm HQ
LOCTITE 406	> 800 ppm HQ	< 50 ppm HQ
LOCTITE 495	> 800 ppm HQ	< 50 ppm HQ
LOCTITE 454	> 800 ppm HQ > 2200 ppm MMBP	< 50 ppm HQ < 100 ppm MMBP
LOCTITE 3090	> 800 ppm HQ > 2200 ppm MMBP	< 50 ppm HQ < 100 ppm MMBP
LOCTITE 3092	> 800 ppm HQ > 2200 ppm MMBP	< 50 ppm HQ < 100 ppm MMBP

compliance through the manufacturing process. It is important to note that although these ingredients are no longer part of the LOCTITE® product formula, trace amounts are possible due to shared manufacturing processes and/or select raw material impurities. Hence, Henkel has taken the additional step of introducing a low specification level for these (<50 ppm for HQ and <100 ppm for MMBP) and each batch is now checked for this after manufacture.

The impact upon the SDS of these upgrades will vary depending on the product and the global region due to different regulations per country/region. Table 5 provides an example of the current versus upgraded formula impact on the European SDS for LOCTITE 454™.

TABLE 5. LOCTITE 454 European SDS Impact—Current vs. Upgrade.

EUROPEAN SDS SECTION	CURRENT LOCTITE 454	UPGRADED LOCTITE 454
3	Composition/information on ingredients identifies both HQ and MMBP	Ethyl cyanoacrylate is the only hazardous chemical mentioned in Section 3
8	Exposure controls/personal protection due to HQ	OELs* associated with HQ are removed from here
11	Toxicological information shown relating to HQ	Toxicological information associated with HQ is removed
12	Ecological information shown relating to HQ	Ecological information associated with HQ is removed

*OEL=Occupational Exposure Limits.

A key requirement of the program was to maintain the existing performance of the LOCTITE products. Extensive validation was carried out to ensure that product performance was not compromised based on these upgrades. Detailed data packages were developed and are available upon request, and product names and Technical Data Sheets (TDS) will not change because of this upgrade. A sample of this validation data is provided for LOCTITE 401™ in Tables 6 and 7.

TABLE 6. LOCTITE 401 Fixture Time on Various Materials—Current vs. Upgrade.

FIXTURE TIME (IN SECONDS)	CURRENT LOCTITE 401	UPGRADED LOCTITE 401
Steel	< 5	< 5
Aluminum	< 5	< 5
ABS	< 5	< 5
PVC	< 5	< 5
PC	5 to 10	5 to 10
Paper	< 5	< 5

TABLE 7. LOCTITE® 401™ Lap Shear Strength on Various Materials—Current vs. Upgrade.

LAP SHEAR STRENGTH (N/MM²)	CURRENT LOCTITE 401	UPGRADED LOCTITE 401
ABS	7 (SF)	7 (SF)
PVC	7 (SF)	6.7 (SF)
PC	10.5 (SF)	10.1 (SF)
Grit-Blasted Mild Steel	20	20.2
Aluminum	12.4	12.5

SF=Substrate Failure (noted for all plastics tested).

LOCTITE ACCELERATORS

Instant adhesive accelerators, which are typically solvent-based products containing one or more active ingredients, are used in certain situations to achieve desirable performance. For example, while instant adhesives are generally known for extremely fast fixturing, their curing speed may still be unsatisfying if the substrate is acidic, or if humidity in the environment is low. Accelerators (such as LOCTITE SF 7452™ and SF 7455™) can be brushed or sprayed onto the surface of parts to be bonded to increase curing speed. Accelerators can be also post-applied over the exposed adhesive after parts are bonded. This “post-activation” method is quite often used in unique applications such as securing wires or coils to printed circuit boards.

DMPT has long been used as a very effective instant adhesive cure accelerator in both pre- and post-applied applications. However, the classification of this material as H350 (may cause cancer under GHS), meant that this ingredient was no longer desirable for use in LOCTITE SF 7452 and SF 7455. An extensive screening program was initiated, and suitable replacement materials were identified which would remove the requirement to have the H350 hazard statement on the product label.

These changes to the formulation have had very positive impacts on the labelling of the LOCTITE Instant Adhesive accelerators. The changes to the hazard pictograms which appear on the label are shown in Table 8.

TABLE 8. European Label Pictograms for LOCTITE Accelerators and Primers.

HENKEL PRODUCT	CURRENT PRODUCT PICTOGRAMS	UPGRADED PRODUCT PICTOGRAMS
LOCTITE SF 7452™		
LOCTITE SF 7455™*		

*Applies to aerosol version(s) of LOCTITE SF 7455.

In the case of the upgraded accelerators the requirement was to ensure that performance was also maintained when used in conjunction with LOCTITE Instant Adhesives. Additional data is available upon request via the previously mentioned Data Packs.

Based on these formulation upgrades, some minor changes will appear on the product Technical Data Sheets (TDS) and are highlighted in Tables 9 and 10.

TABLE 9. LOCTITE Accelerator SF 7452™ Select TDS Properties—Current vs. Upgrade.

TDS PROPERTIES	CURRENT LOCTITE SF 7452	UPGRADED LOCTITE SF 7452
Solvent	Acetone	Acetone
Appearance	Transparent colorless to slightly amber liquid	
Active Ingredient	Amine	Organic disulfide
Fixture Time Grit-Blasted Steel with LOCTITE 416™ (sec)	≤ 10	≤ 10
Flash Off Time (sec)	≤ 30	≤ 30
On Part Life (min)	< 1	5

TABLE 10. LOCTITE Accelerator SF 7455™ Select TDS Properties—Current vs. Upgrade.

TDS PROPERTIES	CURRENT LOCTITE SF 7455	UPGRADED LOCTITE SF 7455
Solvent	Heptane	Heptane
Appearance	Transparent colorless to slightly amber liquid	
Active Ingredient	Amine	Sulfenamide
Fixture Time Grit-Blasted Steel with LOCTITE 416 (sec)	≤ 10	≤ 10
Flash Off Time (sec)	≤ 30	≤ 30
On Part Life (min)	< 1	5

CONCLUSION

As part of Henkel's commitment to continuous improvement, a new line of LOCTITE® Instant Adhesive solutions has been developed with the goal of reducing hazardous chemicals. By identifying and removing chemicals designated under GHS (Globally Harmonized System of Classification and Labeling of Chemicals) as CMRs, these upgraded instant adhesive solutions improve occupational safety—thus enabling users to work more safely. The upgrades have been accomplished with no significant impact on product performance or shelf-life. These innovations in instant adhesives and accelerators combine updated formulations with the high-quality and reliability for which the LOCTITE brand is known.

APPENDIX 1. Detailed Hazard Classification & Statements for All Chemicals Removed from the Formulations.

HYDROQUINONE (CAS 123-31-9)

HAZARD CLASSIFICATION	HAZARD STATEMENT
Acute Tox. Category 4; Oral	H302 Harmful if swallowed.
Skin Sensitizer. Category 1	H317 May cause an allergic skin reaction.
Eye Dam. Category 1	H318 Causes serious eye damage.
Mutagenic Category 2	H341 Suspected of causing genetic defects.
Carcinogenic Category 2	H351 Suspected of causing cancer.
Aquatic Acute Hazard Category 1	H400 Very toxic to aquatic life.
Aquatic Chronic Category 1	H410 Very toxic to aquatic life with long-lasting effects.

MMBP (CAS 119-47-1)

HAZARD CLASSIFICATION	HAZARD STATEMENT
Toxic to Reproduction, Category 2	H361 Suspected of damaging fertility or the unborn child.

DMPT (CAS 99-97-8)

HAZARD CLASSIFICATION	HAZARD STATEMENT
Acute Tox. Category 3; Oral	H301 Toxic if swallowed.
Acute Tox. Category 3; Dermal	H311 Toxic in contact with skin.
Acute Tox. Category 3; Inhalation	H331 Toxic if inhaled.
STOT Respiratory Category 2	H373 May cause damage through prolonged or repeated exposure if inhaled.
Carcinogenic Category 2	H350 May cause cancer.
Aquatic Chronic Category 3	H412 Harmful to aquatic life with long-lasting effects.

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