QUALITY BALANCES.

Winemaking process with ion exchange resin technology

Lewatit®

QUALITY WORKS.

LANXESS
Energizing Chemistry

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WINEMAKING PROCESS WITH ION EXCHANGE RESIN TECHNOLOGY

RED OR WHITE WINE,
WHAT MAKES THE DIFFERENCE?

Introduction

Winemaking is a natural process, but each winery applies different techniques to the winemaking process. This process consists of five basic components:

- Harvesting
- Crushing and pressing
- Fermentation
- Clarification
- Aging and bottling

All in all, vinification is a complex process due to the fact that the quality and attributes of grapes can change from year to year based on weather conditions. To ensure that the quality of the product is consistently high, winemakers can use certain tools in their production process.

In 2014, the OIV Code of Oenological Practices updated its list of accepted processes and their use in must and wine. Summarizing the information provided by these OIV practices, the main applications of membrane and ion exchange technologies in the wine industry are:

- Wine (and must) filtration
- Must concentration
- Alcohol management (including sugar reduction)
- Tartrate stabilization
- pH and acidity management
- Volatile acidity removal
- Dissolved gas management

Winemaking process

Grapes are the only fruit that has the necessary acids, esters, and tannins that give wine its typical taste. Tannins, for example, are textural elements that make the wine dry and add bitterness and astringency to the wine. The traditional vinification process distinguishes between the final product, i. e., red or white wine.

Mechanical presses stomp or trod the grapes into must. For red wine, a must consisting of grape juice and grape skin is prepared. In contrast, white wine preparation involves only the grape juice being fermented.

During the dry wine fermentation process, all sugar is converted into ethanol and carbon dioxide. To create a sweet wine, winemakers will sometimes stop the process before all of the sugar is converted. Very often a second process known as lactic acid fermentation takes place to adjust the overall sensory profile of the wine. Fermentation can take from ten days to one month or longer.

Once the fermentation is completed, the liquid and solid parts must be separated and the microorganisms removed. In most cases, this is done via micro- or ultrafiltration. Additionally, sulfur dioxide can be added to ensure microbiological stability and protect the wine against oxidation. After the wine has matured in storage tanks or barrels, another clarification and filtration step is required to remove undesired components. The final step is the bottling process.

EVERYTHING STARTS WITH SAVORY GRAPE MUST

Grape must stabilization

Ion exchange is especially useful for stabilizing grape must or wine by removing salts, organic acids, nitrogenous compounds such as proteins, and color bodies such as polyphenols. Unstable proteins and phenolics found in grape must can form a haze in the grape must or wine after bottling. Grape must used in the production of white wine, where clarity and color are important aspects of a wine's character, pose a special concern with regard to haze formation.

Studies have shown that haze formation in beverages is related to the concentration and ratio of haze-active proteins and polyphenols. Bentonite fining or ultrafiltration is not always effective in removing protein fragments. Ion exchange resins/adsorbers have shown to be an effective method of removing salts, reducing free acidity, organic acids, and color bodies, and reducing haze-forming precursors.

The grape must correction process itself is identical with MCR production, which is described in detail in the next section. After demineralization (= decationization and deanionization) and decolorization with ion exchange processes, concentration with membrane technology is not required. The refined grape must proceeds directly to the fermentation step.

Lewatit® products for grape must stabilization:

- Lewatit® S 1568
- Lewatit® S 1668
- Lewatit® S 2568
- Lewatit® S 4528
- Lewatit® S 5128
- Lewatit® S 6368 A
- Lewatit® S 7968

Rectified concentrated must = MCR (*mosto concentrato rettificato*)

The alcohol level in wine is directly related to the amount of sugar in the must, which is clearly a function of the amount of sugar in the original grapes. Sugar is transformed into alcohol and CO_2 by fermentation. The amount of sugar in grapes can be too low to make a wine with a sufficient level of alcohol if the weather conditions are not right. In many countries it is forbidden to add sugar (saccharose) to the must before fermentation, a process also referred to as chaptalization. Adding a liquid, natural concentrated sugar obtained from the same grapes is permitted and regulated, e.g., within the EU.

MCR (*Mosto concentrato rettificato*), Italian for "rectified concentrated must," is the product that is permitted to increase the sugar level of the must without affecting the organoleptic characteristics of the resulting wine. MCR is a clear, liquid, concentrated grape-sugar solution with a very light and pleasant flavor, obtained by filtration, demineralization, decolorization, and concentration of fresh or muted must. Demineralization and decolorization are typical ion exchange processes, whereas concentration is achieved with membrane technology.

Raw grape must contains all salts (mainly potassium salts), organic acids (mainly tartaric acid), sugars (e.g., glucose and fructose), color bodies (polyphenols and anthocyanins), and flavoring agents typical of the original grapes. Muted must also contains sulfur dioxide, deliberately added to prevent fermentation.

pH adjustment can be done after deanionization with a buffer column operating under the same conditions as the decationization step.

An adsorber resin like Lewatit® S 7968 may be used as a final polisher to reduce color, odor, and haze-forming materials.

- Operating condition: 20–30°C, 3–5 BV/hr
- Regeneration condition: 20–30°C, 2 BV/hr
- Regenerant: 4% NaOH 40–60 g/l_{Resin}, 0.5% HCl 20–40 g/l_{Resin}

During the regeneration of the decolorization step, an extraction of color bodies from grape must fulfills the demand for "natural colors" coming from the food and pharmaceutical industries.

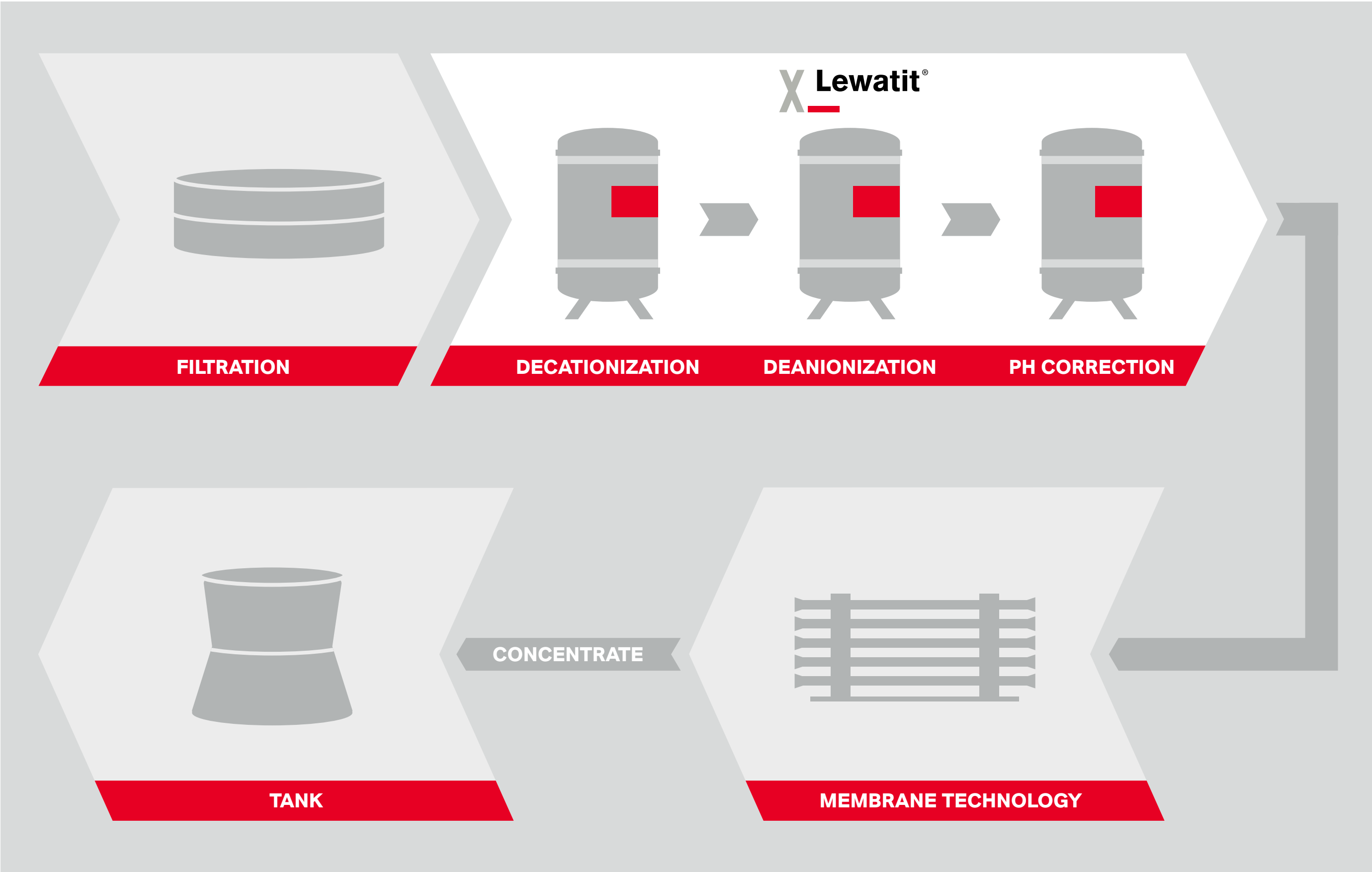

Figure 1 illustrates the treatment schemes being utilized to treat grape must for MCR production.

Lewatit® products and process steps for MCR

Application	Decationization	Deanionization	pH correction
	Lewatit® S 1568 **Lewatit® S 1668** **Lewatit® S 2568**	**Lewatit® S 4528** **Lewatit® S 5128** **Lewatit® S 6368 A**	**Lewatit® S 1568** **Lewatit® S 1668** **Lewatit® S 2568**
Regenerant	HCl	NaOH	HCl
Quantity (g/l_{Resin}) co-current	80–100	WBA 60–80 SBA 100	80–100
Quantity (g/l_{Resin}) countercurrent	55–65	WBA 50–60 SBA 40–50	55–65
Flow rate (BV/hr) exhaustion	3–20	3–20	3–20
Flow rate (BV/hr) regeneration	2	2	2
Temperature (°C) exhaustion	20–30	20–30	20–30
Temperature (°C) regeneration	20–30	20–30	20–30
Capacity (eq/L)	0.9–1.2	0.8/0.4	0.9–1.2

WBA = weak base anion resin / SBA = strong base anion resin

THE RIGHT COMPOSITION MAKES IT DELICIOUS

Wine correction

During the aging process of the wine, the concentration of acids and compounds that negatively impact the wine's taste may increase. The alcohol content may also rise above the requested level. To rejuvenate the wine (lifting) or improve the taste profile of the wine, membrane technology and ion exchange processes can be used to remove undesired compounds.

Tartrate stabilization

The pH of wine is important to know as it plays a critical role in many aspects of winemaking, in particular concerning wine stability. According to Boulton et al. (1999), pH influences microbiological stability, affects the equilibrium of tartrate salts, determines the effectiveness of sulfur dioxide and enzyme additions, influences the solubility of proteins and effectiveness of bentonite, and affects red wine color and oxidative and browning reactions.

For the tartaric stabilization (removal of potassium ions), we recommend either the cation exchanger Lewatit® S 1568 or the Lewatit® S 1668, which are particularly suitable for use in the drinking water and food sector. For potassium removal, it is possible to use the exchanger loaded either with hydrogen ions or sodium ions. The wine either becomes acidic (release of H ions) or it remains unchanged in pH (release of Na ions). If a mixed regeneration process is used (with hydrochloric acid and saline solution), one can achieve an intermediate state by any change in the amount of regenerant.

In addition to potassium removal, a change in the calcium and magnesium content occurs, but this reaction is very different from wine to wine because of the complex formation of these ions. Ion exchange for wine stabilization is permitted only in some countries specifying the types of resins, the ionic form, and the specification for the treated wines.

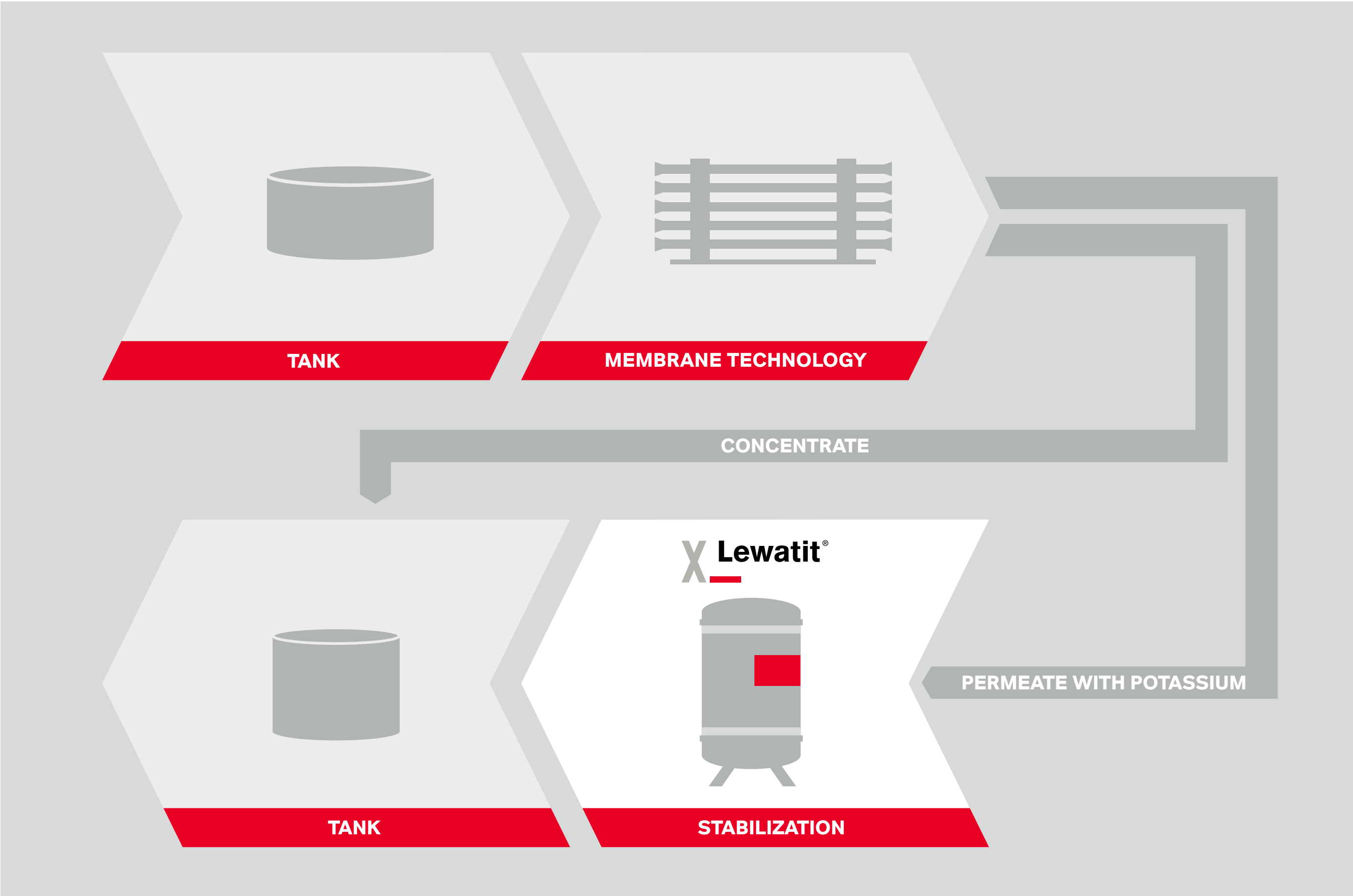

Figure 2 illustrates the treatment schemes being utilized for wine stabilization.

Lewatit® products for wine correction

Application	Stabilization
	Lewatit® S 1568 **Lewatit® S 1668**
Regenerant	NaCl (HCl)
Quantity (g/l_{Resin}) co-current	80–100
Quantity (g/l_{Resin}) countercurrent	55–65
Flow rate (BV/hr) exhaustion	5–20
Flow rate (BV/hr) regeneration	3
Temperature (°C) exhaustion	20–30
Temperature (°C) regeneration	20–30
Capacity (eq/L)	1.0–1.4

NOT ALL ACIDS ARE WELCOME

Wine deacidification

The acid concentration (titratable acid) in wine is expressed in grams of acid per 100 ml of wine with titratable acid being calculated as if all the acids found in the wine are tartaric acid. Normally, most finished table wines will have an acid content ranging between 0.50 and 0.80 percent. Most of the acids found in sound wines (tartaric, malic, citric, succinic, and lactic) are fixed acids, which originate in the grape juice, remain throughout the fermentation process, and add to the style, balance, and taste of the finished wine. Tartaric and malic acids are the major wine acids and are present when the grapes are first picked. Tartaric acid is the strongest of the grape acids. It is responsible for much of the tart taste of the wine and contributes to the biological stability and longevity of the wine. Malic acid is much weaker than tartaric acid. It is more biologically unstable and easily metabolized by various types of wine bacteria. Both of these fixed acids are nonvolatile and add very little odor to the wine. Fixed acids like tartaric and malic acids have low vapor pressures, which relates to their characteristic of having no significant odor in wine.

Acetic acid is significantly different from the fixed acids found in wine in that it has a high vapor pressure (high volatility), which can add a distinctive vinegar odor to the wine. Sound wines normally contain very little acetic acid, however, acetic acid can form in the wine through several different pathways, which may include:

- Formed by yeast during fermentation
- ML fermentation, citric acid fermentation
- Stuck fermentation – lactic bacteria convert residual sugars to acetic acid
- In the presence of air, vinegar bacteria can convert ethyl alcohol into large quantities of acetic acid

All of the above processes can contribute to the formation of acetic acid in wine. Small amounts of acetic acid can enhance the bouquet of the wine by producing a somewhat sour essence to the taste of the wine, however, excessive amounts of acetic acid can cause an accentuated sharpness or sourness, and in extreme cases turn wine into vinegar. Although the spoilage of wine due to the inadvertent formation of acetic acid in the wine can be devastating, the use of ion exchange resins for the deacidification of wine has proven to be an effective method of recovering wine that has become spoiled.

To remove interfering amounts of acids (including tartrate) from wine, we recommend Lewatit® S 5128, Lewatit® S 5221, or Lewatit® S 4528. These resins are especially suitable for removing weak acids. They are added to the wine as part of the "batch process". The quantity of exchanger to be used per liter of wine must be determined by experiment. According to the selective series, the binding of anions to the exchanger decreases as follows: H_2SO_4 > H_3PO_4 > tartaric acid > malic acid > citric acid > lactic acid > succinic acid > acetic acid.

In his 2016 master's thesis, Cotea compared the ion exchange resins Lewatit® S 5221, Lewatit® S 5128, and Lewatit® S 4528 using model solutions of various wine acids in distilled water, model solutions of acetic acid at different concentrations in model solutions with either ethanol or sugar content to mimic either a wine or a grape must environment. For more details, refer to Cotea's master's thesis (2016). The first use of resin may also bind flavoring molecules of the wine. This will decrease with repeated use.

Lewatit® products and process steps for wine deacidification

Application	Deacidification with WBA	Deacidification with SBA
	Lewatit® S 4528 **Lewatit® S 5221**	**Lewatit® S 5128**
Regenerant	NaOH	NaOH
Quantity (g/l_{Resin}) co-current	60–80/120–160	60–80
Quantity (g/l_{Resin}) countercurrent	50–60/100–120	50–60
Flow rate (BV/hr) exhaustion	5–20	5–20
Flow rate (BV/hr) regeneration	3	3
Temperature (°C) exhaustion	20–30	20–30
Temperature (°C) regeneration	20–30	20–30
Capacity (eq/L)	0.8/1.8	0.8

Wine bottling

The wine is passed through a micro- or ultrafiltration membrane to remove any particles formed during maturation in a barrel and all critical microorganisms that could cause refermentation and a change in the sensorial attributes of the final product.

Before bottling, Velcorin® can be applied to ensure the microbiological stability of the wine. Velcorin® helps winemakers avoid being surprised by bad wine quality at the end of the process, particularly when it comes to aging sweet and soft wines or wine-based beverages. Whether red or white, rosé, or a traditional Spanish tinto de verano, a mixture of red wine and lemonade: LANXESS has been helping wine producers worldwide to maintain the typical character of their products for more than 30 years.

LANXESS PRODUCTS MAKE WINE UNIQUE

Characteristics of Lewatit® products

Product	Product matrix	Ionic form	Shipping weight (g/l) +/– 5%	Bead size (mm)*	Uniformity coefficient max.	Total capacity (eq/l) min.	Volume change (%) max.	Water retention (%)
Strong Acidic Cation (SAC)								
Lewatit® S 1568	Styrene/DVB gel	Na+	810	MD: 0.60 (+/– 0.05)	1.1	1.8	12 (Na+ → H+)	45–50
Lewatit® S 1668	Styrene/DVB gel	Na+	830	MD: 0.62 (+/– 0.05)	1.1	2.2	12 (Na+ → H+)	41–46
Lewatit® S 2568	Styrene/DVB macroporous	Na+	740	MD: 0.65 (+/– 0.05)	1.1	1.7	10 (Na+ → H+)	50–55
Weak Base Anion (WBA)								
Lewatit® S 4528	Styrene/DVB macroporous	FB	620	HD: 0.4–1.25	1.6	1.7	48 (FB → Cl^-)	620
Lewatit® S 5221	Polyacrylate macroporous	FB	740	HD: 0.4–1.6	1.8	2.8	26 (FB → Cl^-)	740
Strong Base Anion (SBA) – Type I								
Lewatit® S 5128	Polyacrylate gel	Cl^-	730	HD: 0.4–1.6	1.8	1.35	25 (Cl^- → OH^-)	48–55
Lewatit® S 6368 A	Styrene/DVB macroporous	Cl^-	600	MD: 0.62 (+/– 0.05)	1.1	1.0	22 (Cl^- → OH^-)	60–65

Product	Product matrix	Ionic form	Shipping weight (g/l) +/– 5%	Bead size (mm)*	Uniformity coefficient max.	Surface BET (m^2/g) approx.	Pore volume (cm^3/g) approx.	Water retention (%)
Adsorber								
Lewatit® S 7968	Styrene/DVB macroporous	None	600	MD: 0.49 (+/– 0.05)	1.1	800	1.2	54–63

***** Monodisperse (MD, mean value), heterodisperse (HD, share > 90%).

Further details are provided in the technical product data sheets, which are available at **www.lanxess.com**.

The special properties of Lewatit® products can only be fully utilized if the technology and process used correspond to the current state of the art. Further advice in this matter can be obtained from LANXESS. If using Lewatit® products with solutions listed above, special attention should be given to the initial cycles of the new resin. Please refer to the recommended start-up conditions, which are available on request.

References

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Gindorf, Laura, "Use of cation exchange resins for acidification and tartaric stabilization of wine," bachelor's thesis, Hochschule Geisenheim University 2018

Röcker, Jessica (et al.), "The use of glucose oxidase and catalase for the enzymatic reduction of the potential ethanol content in wine," Food Chemistry 210 (2016) 660–670

Boulton, Roger B. (et al.), "Principles and Practices of Winemaking," (1999) ISBN: 978-1-4419-5190-8

Health and safety information

Appropriate literature has been assembled which provides information concerning the health and safety precautions that must be observed when handling the LANXESS products mentioned in this publication. For materials mentioned which are not LANXESS products, appropriate industrial hygiene and other safety precautions recommended by their manufacturers should be followed. Before working with any of these products, you must read and become familiar with the available information on their hazards, proper use and handling. This cannot be overemphasized. Information is available in several forms, e. g., material safety data sheets, product information and product labels. Consult your LANXESS representative in Germany or contact the Health, Safety, Environment and Quality Department (HSEQ) of LANXESS Germany or – for business in the USA - the LANXESS Product Safety and Regulatory Affairs Department in Pittsburgh, PA.

Regulatory Compliance Information:

Some of the end uses of the products described in this publication must comply with applicable regulations, such as the FDA, BfR, NSF, USDA, and CPSC. If you have any questions on the regulatory status of these products, contact your LANXESS Corporation representative, the LANXESS Regulatory Affairs Manager in Pittsburgh, PA or the Health, Safety, Environment and Quality Department (HSEQ) of LANXESS Deutschland GmbH in Germany. The manner in which you use and the purpose to which you put and utilize our products, technical assistance and information (whether verbal, written or by way of production evaluations), including any suggested formulations and recommendations are beyond our control. Therefore, it is imperative that you test our products, technical assistance and information to determine to your own satisfaction whether they are suitable for your intended uses and applications. This application-specific analysis must at least include testing to determine suitability from a technical as well as health, safety, and environmental standpoint. Such testing has not necessarily been done by us. Unless we otherwise agree in writing, all products are sold strictly pursuant to the terms of our standard conditions of sale. All information and technical assistance is given without warranty or guarantee and is subject to change without notice. It is expressly understood and agreed that you assume and hereby expressly release us from all liability, in tort, contract or otherwise, incurred in connection with the use of our products, technical assistance, and information. Any statement or recommendation not contained herein is unauthorized and shall not bind us. Nothing herein shall be construed as a recommendation to use any product in conflict with patents covering any material or its use. No license is implied or in fact granted under the claims of any patent.

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