

INTRODUCTION

MILLAD 3988 is a breakthrough clarifying agent technology for polypropylene (PP). Use of this additive in properly formulated and processed PP gives improved transparency, increased resin throughput, productivity gains and enhanced physical properties.

The versatility and relatively low cost of PP have historically made it a polymer of choice, except where its benefits were overshadowed by its haziness. Now with the exceptional clarity possible using MILLAD 3988, PP has become an increasingly popular option in many applications where aesthetics are an important design consideration. PP clarified with MILLAD 3988 gives product planners remarkable flexibility in design, packaging and material selections.

THE BENEFITS OF PP CLARIFIED WITH MILLAD 3988

- ***Clearest PP Possible***

The highest clarity, gloss and surface smoothness available.

- ***Increased Productivity***

PP with MILLAD 3988 gives higher throughput and productivity.

- ***Cost Efficiency***

The cost efficiency of PP, combined with its low density, makes it an attractive alternative to other resins.

- ***Versatility***

PP clarified with MILLAD 3988 offers an excellent combination of properties – toughness, flexibility, rigidity, moisture barrier, chemical resistance, heat resistance, and suitability for food contact.

- ***Improved Properties***

PP clarified with MILLAD 3988 offers improved physical properties vs unclarified PP – particularly higher stiffness and heat distortion temperature.

- ***Broad Processability***

MILLAD 3988 does not plate-out on cooling surfaces and it doesn't produce objectionable odors during processing.

- ***Ideal for Food Contact Applications***

MILLAD 3988 in PP does not affect the taste of contained foods or liquids.

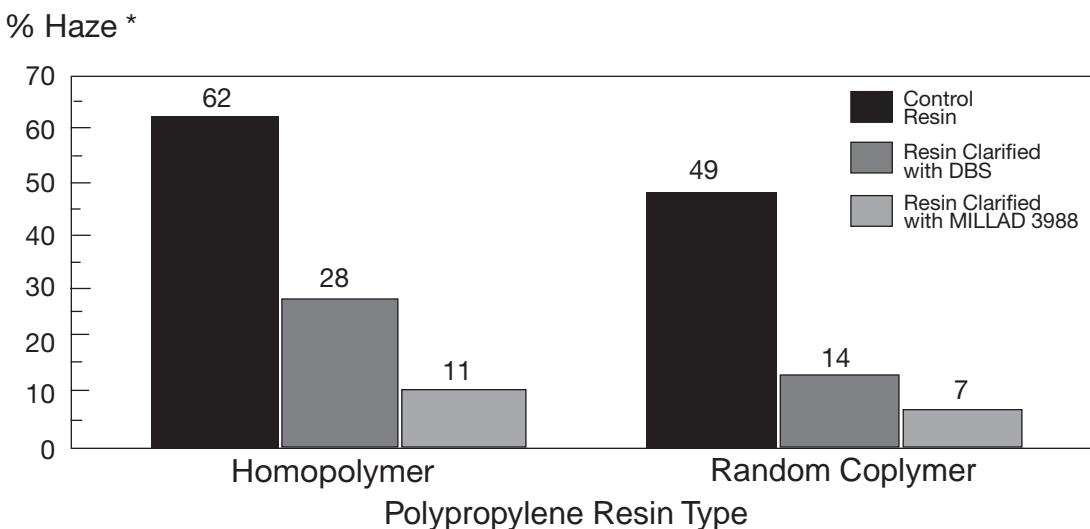
HOW MILLAD® 3988 WORKS

PP normally crystallizes slowly into relatively large crystals known as spherulites. These spherulites, larger than the wavelength of visible light, refract light. This reduces clarity and increases haze. When PP is clarified with MILLAD 3988, the rate of crystal initiation is increased by many orders of magnitude throughout the polymer. Because many more crystals are growing in the same amount of space, they are all much smaller in size. The result is crystals smaller than the wavelength of visible light that allow light to pass through, imparting enhanced clarity.

HOW CLEAR IS PP WITH MILLAD 3988

MILLAD 3988 gives enhanced clarity over other commercially available clarifiers like dibenzylidene sorbitol (DBS or Millad 3905). The following graph illustrates the typical % haze improvements in injection molded plaques of homopolymer and random copolymer PP's containing MILLAD 3988.

**% Haze Reduction of Polypropylene
When Clarified with MILLAD 3988**



*Hazemeter measurement on 1.27 mm (50 mil) plaques in 12 MF injection molding grades with standard co-additive packages.
Note: Clarity and % haze are resin and processing dependent

OBTAINING RESINS CLARIFIED WITH MILLAD 3988

The easiest way to use PP clarified with MILLAD 3988 is to obtain a resin from your PP supplier. The clarifier is usually added by the PP manufacturer to the resin during compounding. A broad range of high quality resins which contain MILLAD 3988 are available worldwide from leading polypropylene manufacturers.

Milliken Chemical can provide specific information concerning commercially available resins for all types of fabrication processes.

COMPARISON OF PP WITH MILLAD® 3988 TO OTHER MATERIALS

PP clarified with MILLAD 3988 has many benefits compared to other materials – light weight, strength and cost effectiveness, to name a few. A comparison of some of the properties of PP with MILLAD 3988 are summarized below. This is a matrix format comparing PP with MILLAD 3988 versus polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC), high density polyethylene (HDPE), polycarbonate (PC) and glass (GLS):

Desired Property	Other Material Choices					
	PET	PS	PVC	HDPE	PC	GLS
See Through Transparency and Gloss	○	○	○	++	○	○
Cost/Unit Volume	++	+	+	○	++	+
Hot Filling Capacity	++	++	++	++	○	○
Moisture/Vapor Barrier	+	++	+	○	++	-
Lower Density	++	+	++	○	++	++
Taste & Odor Transfer Properties	+	○	+	+	○	-
Drop Impact Strength	+	++	-	-	-	++
Flexibility	○	++	○	○	○	++
Stiffness	-	-	-	+	-	-
Chemical Resistance	+	+	++	○	○	○
Oxygen Barrier	-	○	-	-	○	-

Key – PP with MILLAD 3988 is: Much Better (++), Better (+), Comparable(○), Worse (-)

PROCESSING RESINS CONTAINING MILLAD 3988

Resins containing MILLAD 3988 can be used in all fabrication processes – injection molding, blow molding (EBM, IBM, ISBM, SBM), sheet extrusion, thermoforming and extrusion of film or fiber. In general, PP with MILLAD 3988 will be very robust in processing – that is it will have a wide temperature range for processing – as compared to conventional clarified PP.

Because Millad 3988 is both a powerful nucleating agent and clarifying agent, resin solidification occurs significantly faster than a standard resin. This results in higher throughput over non-nucleated PP in most processing operations. Equipment parameters are normally adjusted to take advantage of this improvement and to insure trouble free processing.

Some general recommendations follow on the next page:

PROCESSING...CONTINUED

INJECTION MOLDING

Resins containing MILLAD® 3988 may be processed over a wide temperature range. Nominal melt temperatures of 390°-520°F (200-270°C) can be used. Maximum clarity is usually obtained when mold temperatures are between 70-100°F (20-40°C) and the mold surface is smooth and polished (SPI 1-2 finish recommended, SPI 3 finish is normally acceptable).

The table below addresses several process opportunities that could be encountered with PP containing MILLAD 3988 as compared to PP containing previous generation clarifiers or a non-nucleated PP.

OPPORTUNITY	CAUSES	SOLUTIONS
Incomplete mold fill, voids, bubbles.	<ul style="list-style-type: none"> •Rapid resin set-up may not allow for complete mold fill or degassing. 	<ul style="list-style-type: none"> •Increase melt temperature. •Increase mold temperature •Insure mold vents are not plugged.
Flow Lines	<ul style="list-style-type: none"> •Undersized equipment relative to the mold. •Poor mixing and/or short residence times. •Poor melt homogeneity. •Note: Flow lines form because a polymer band freezes faster than the surrounding polymer and is forced to move as the mold fills. This results in a hazy line that follows the mold flow. 	<ul style="list-style-type: none"> •Increase back pressure to raise the melt temperature and improve melt temperature homogeneity through longer mixing. •Increase barrel and/or mold temperature settings to allow for quicker mold fill prior to polymer freezing. •Utilize mixing nozzles or high performance screws to improve melt homogeneity.
Cycle Time Reduction	<ul style="list-style-type: none"> •Time can be reduced to take advantage of the faster freezing rate. 	<ul style="list-style-type: none"> •Reduce time from cooling cycle if the total cycle is not limited by screw recovery or other parameters.
Clarity Optimization	<ul style="list-style-type: none"> •Cloudiness can be caused by over packing the mold. 	<ul style="list-style-type: none"> •Reduce the injection pressure.

INJECTION STRETCH BLOW MOLDING

There are many types of ISBM and SBM machinery available for manufacturing PP bottles with excellent clarity. This equipment orients the clarified PP and can give glass like clarity. Recommended processing conditions depend on equipment type and the specific resin. Contact your Milliken Chemical technical representative for specific recommendations.

SHEET EXTRUSION

For sheet extrusion, PP containing MILLAD 3988 can be processed up to 520°F (270°C). Because of the rapid increase in crystallization rate, resins with Millad 3988 will process differently than non-nucleated PP. In general - the melt temperature should be adjusted so the "melt curtain" from the die is clear - this is nominally 455-475°F (235-245°C) for homopolymer PP and 435-455°F (225-235°C) for random copolymer PP. The cooling roll temperatures should be adjusted such that the surface temperature of the sheet leaving the three stack roll is below the freezing point of the plastic. The surface of the sheet requires monitoring to insure it is below the PP freezing point - about 230°F (110°C) for homopolymer PP and about 200°F (95°C) for a typical random copolymer. Maintaining the proper sheet temperature exiting the rolls insures the sheet will retain a high polish and surface smoothness when leaving the cooling stacks. The rolls which touch the plastic as it is freezing must have a mirror finish for optimal clarity and freezing should not be completed until both sides of the sheet are polished.

PROCESSING...CONTINUED

SHEET EXTRUSION - CONTINUED

Freezing in the nip should be avoided because it imparts uneven orientation and stress in the sheet. Greater bank stability has been observed in PP with MILLAD® 3988 however a minimum bank height is still recommended to avoid uneven orientation. To insure intimate contact of the sheet to the middle roll, it is essential that the bank distribution and sheet gauge are maintained uniformly from side to side - reducing the tendency of air pockets to form and assuring consistent surface polish. PP with MILLAD 3988 is usually processed at higher roll temperatures than unclarified PP due to its much higher rate of crystallization. Roll temperatures are dependent on resin, sheet thickness and equipment.

MILLAD 3988 is not compatible with other types of nucleators so regrind containing other nucleators should not be blended with the resin containing MILLAD 3988. Normal PP resin melt flow rates in the range of 2-4 can be used. MILLAD 3988 does allow higher MFR resins to be used to manufacture sheet than either nucleated or non-nucleated resins. This is due to the unique mode of action of MILLAD 3988 that gels the molten polymer above its freezing temperature - leading to a much higher melt viscosity.

SOLID PHASE PRESSURE FORMING (SPPF)

Because of its relatively sharp melting point and rapid drop in viscosity above its melting point, PP had traditionally been difficult to thermoform. Recent improvements in processing technologies such as very accurate temperature control systems and plug assisted forming under solid phase conditions have made PP a viable thermoforming material. The addition of MILLAD 3988 to the PP can create parts with exceptional clarity and gloss - giving product designers the option to use PP as a substitute for PS, PET or PVC.

When thermoforming PP with MILLAD 3988 it is very important to control the temperature of the sheet prior to forming. The ideal surface temperature range for forming clarified PP homopolymer is 309-317°F (154-158°C). Random copolymer PP is not as well defined as it is dependent on % ethylene but a surface temperature of 280-286°F (138-141°C) is a good starting point for a nominal 3% ethylene random copolymer. If the sheet is too hot, the clarity of the parts will be poor. If the sheet is too cool, the part wall distribution will be poor. Since many thermoforming lines are not equipped with on-line temperature measurement, a hand held IR probe may be useful when lining out the process.

Unlike other processes, mold finish is not critical and moderately polished aluminum is adequate. However, the surface of the plug must be very smooth to avoid scratching the inside surface of the part. The plug is necessary with PP to insure consistent wall distribution and syntactic foam is an adequate plug material.

Because PP does not go through a freezing or crystallization step when thermoformed, there is no expectation that processing will be faster. It is important to realize that mold temperature can have a big effect on part shrinkage - hot molds give more shrinkage than cold molds. Because it is possible to extrude sheet from PP with MILLAD 3988 at higher melt flows it is also possible to form parts with a higher ultimate elongation that are easier to draw - leading to even better clarity and gloss. Lower melt flow rate resins may be used if parts with higher stiffness and slightly worse clarity are desired.

Although PP does not process more rapidly when clarified with MILLAD 3988, it certainly processes more consistently and easily. Finished part wall distribution is much more consistent when using a clarified PP grade when compared to using a standard nucleated PP grade. The same phenomena that allows the PP sheet to have a higher melt viscosity during extrusion allows PP sheet to lay flatter, have improved sag resistance and have a lower tendency to deform, pucker or wrinkle during reheating. PP sees a 6% thermal expansion during the oven heating phase of the pressure forming process and this expansion can contribute to sag. The MILLAD 3988 inhibits the expanding sheet from creeping, leading to flatter sheet that gives finished parts of exceptional consistency. This allows for lightweighting of finished parts.

PROCESSING...CONTINUED

THIN WALL INJECTION MOLDING (TWIM)

PP Clarified with MILLAD® 3988 is ideal for the TWIM process. Thin wall parts are defined as a wall thickness of less than 0.025 in (0.62 mm) or a flow length to wall thickness ratio of greater than 200. When compared to standard injection molding, high melt flow PP's are used (30-60 MFR), along with accumulator assist injection and higher injection speeds and pressures. Stack molds are common. Melt temperature ranges of 550-610°F (285-320°C) combined with mold temperature ranges of 40-60°F (5-15°C) and highly polished mold surfaces are recommended for the best clarity. Cycle reductions can be realized with PP clarified with MILLAD 3988 versus conventional nucleated PP. The process opportunities encountered in TWIM, when processing PP resins with MILLAD 3988, are very similar to those encountered with standard injection molding with the additions described in the following table:

OPPORTUNITY	CAUSES	SOLUTIONS
Ejection from core or demolding	<ul style="list-style-type: none"> •Rapid resin crystallization causes PP to stick to the core due to in-mold shrinkage. 	<ul style="list-style-type: none"> •Put light draw marks, in the direction of ejection, on the core surface to assist in breaking the vacuum. •Core cap ejection technology has been found to be more effective than air poppets, particularly when molding softer PP's like random copolymers.
Change in part dimensions	<ul style="list-style-type: none"> •Powerful nucleation effect in MILLAD® 3988 	<ul style="list-style-type: none"> •Wait 2 weeks before measuring critical dimensions – shrinkage occurs more rapidly but the final shrinkage is the same compared to other nucleators. •Increasing temperatures increases shrinkage and increasing cooling time decreases shrinkage

END-USE APPLICATIONS FOR PP CLARIFIED WITH MILLAD® 3988

PP with MILLAD 3988 can be used in many applications. Product planners have the flexibility to choose PP clarified or nucleated with MILLAD 3988, in most fabrication processes. Most of the potential end-uses are applications where switching to clarified PP, from other materials, will lead to lower cost or improved functionality. The following table lists just some of the many applications possible using a variety of fabrication processes.

Injection Molding:

- Housewares
- Living hinge storage cases
- Storage boxes
- Medical devices
- Electronic and video boxes
- Protective packaging
- Overcaps
- Appliance parts

Extrusion Blow Molding:

- Ketchup and sauce bottles
- Cleaning product bottles
- Water bottles
- Food & drink bottles

Stretch Blow Molding:

- Water bottles
- Pharmaceutical bottles
- Dry food and spice jars
- Household cleaners
- Isotonic and sports drinks
- Baby bottles
- Housewares
- Liquid soaps and detergents

Sheet Extrusion:

- Sleeves for video cassettes
- Fabricated lunch pails
- Flooring sheet
- Stationary products

Thermoforming:

- Blister packaging
- Medical trays
- Disposable deli trays
- Microwavable fast foods
- Drink cups
- Single serve juice containers
- Dairy case packaging
- Cookie trays

Thin Wall Injection Molding:

- Dairy case containers
- Deli containers
- Disposable drink cups
- Storage containers

Cast Film:

- Photograph album protectors
- Stationary products
- Candy wrappers
- Medical films

Nucleation in Various Processes:

- BOPP film
- Non-wovens
- Block copolymers and TPO's
- Faster cycles or stiffer products

REGULATORY CLEARANCES

MILLAD® 3988 is cleared for use by numerous regulatory agencies in countries worldwide. A partial list includes the FDA (United States Food and Drug Administration), HPB (Canadian Health Protection Board) and BGA (Bundesgesundheitsamtes – German Food Clearance), to name a few. In addition MILLAD 3988 is a registered article of commerce in most countries. A current regulatory clearance summary is available from your Milliken Chemical Technical Representative upon request.



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