# PROCESSING GUIDELINES

## for TUBALL™ MATRIX 601/ 602

for Liquid Silicones

## Contents

# 1. DILUTION PRINCIPLES

Uniform distribution of TUBALL™ MATRIX in the silicone plays a key role in enhancing the electrical conductivity of the final compound. In order to obtain a high-quality TUBALL™ MATRIX dispersion, OCSiAl recommends that close attention be paid to the dilution procedure.

- The resistivity level achieved will depend on the loading of TUBALL™ MATRIX. The target dosage of TUBALL™ MATRIX refers to the loading in the whole silicone formulation by weight.
- The mixing time, number of mixing cycles and mixing speed may need to be adapted for different machinery size/type to obtain a final mixture that is homogeneous.
- The dilution ratio depends on the required level of resistivity and the loading of TUBALL™ MATRIX.

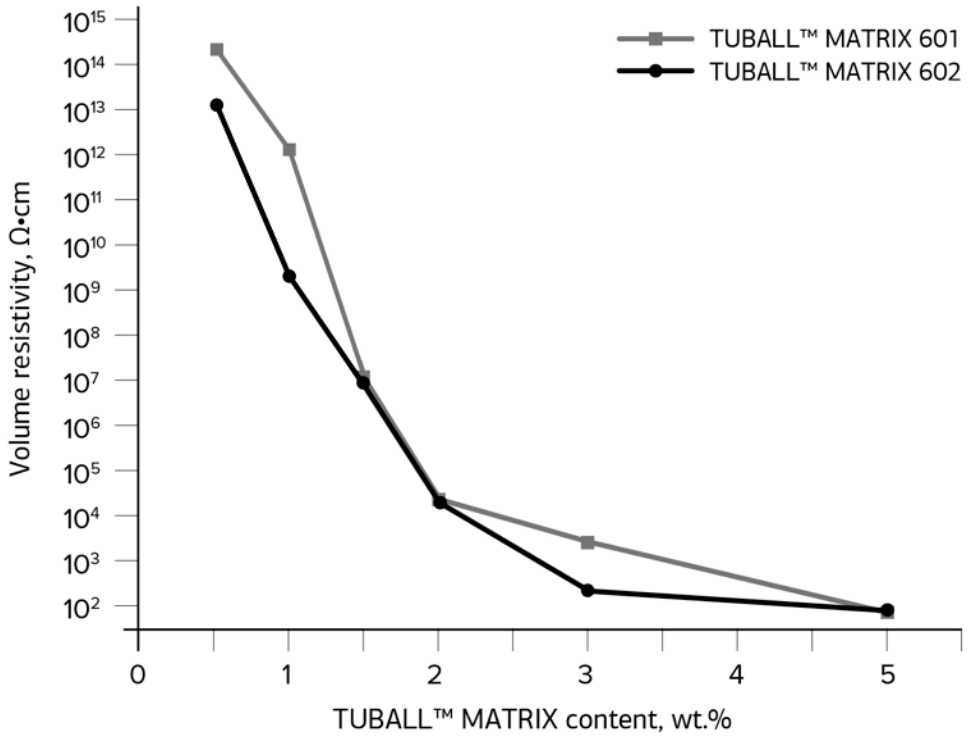



**Figure 1.** Volume resistivity of 30 Hardness LSR silicone (SQUARE® LIM 3900-30A/B, Viscosity 600 000 cPs) with TUBALL™ MATRIX 601 & 602 in the range $10^2$–$10^{14}$ Ω·cm (sample shape: compression-moulded rubber sheet of 2 mm thickness)

For LSR with initial viscosity **more than 200 000 mPa*s** and **TUBALL™ MATRIX** content of more than 1.5%, dilution can be done in one step (Direct mixing). In case of **TUBALL™ MATRIX** content of 1.5% or less, achieving the highest quality of **TUBALL™ MATRIX** dispersion in the final compound requires a two-stage dilution procedure (Premix).

For LSR\RTV with initial **viscosity less than 200 000 mPa*s only Direct mixing could be used**, please refer to Section 2 – Dilution with High speed mixer.

**Key principles of dispersion of TUBALL™ MATRIX:**

The dispersion quality depends strongly on two factors:

a) the mechanical dispersion characteristics (shear forces during the compounding):
- type of machinery
- mixing modes

b) the carrier compatibility:
- viscosity of silicone base.

TUBALL™ MATRIX 601/602 is a low viscous carrier based masterbatches and thus the best compatibility is achieved with LSR & RTV in the hardness range from 20 to 50 Shore A.

The number of cycles may vary depending on the type of three-roll mill (TRM) and the carrier media. Milling should be continued until the size of agglomerates has reduced to a constant value. In Figure 2 it may be seen how electrical conductivity, number of cycles and viscosity of TUBALL™ MATRIX distribution correlate. Plotting such graph allows to choose an optimal number of cycles.

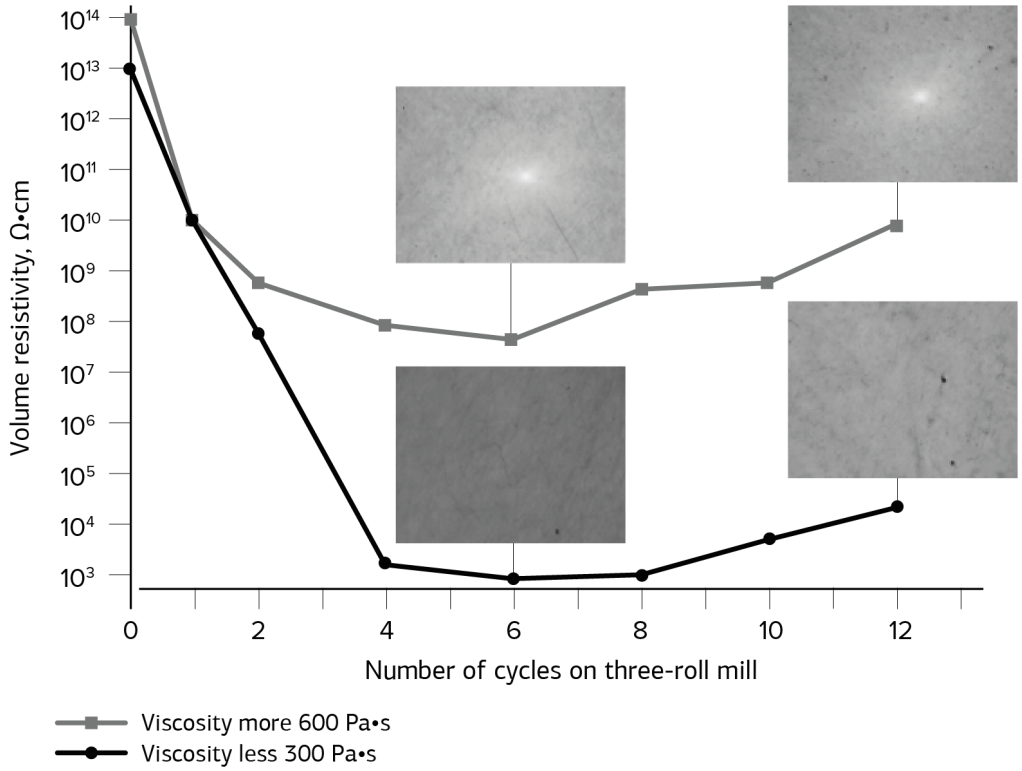



**Figure 2.** Volume resistivity of different viscosity silicones as function of number of cycle mixing on three roll mill (TRM) (1.5% TUBALL™ MATRIX 601)

# 2. DILUTION PROCEDURE IN LOW VISCOUS SILICONES (<50 000 mPa·s)

If the basic material has a low viscosity (up to 50 000 mPa·s), it can be mixed using an overhead stirrer (when the concentration of the **TUBALL™ MATRIX** is not more than 3%).

**! NOTE. If the loading of TUBALL™ MATRIX is higher than 3%, please refer to the section 3 Dilution with three-roll mill.**

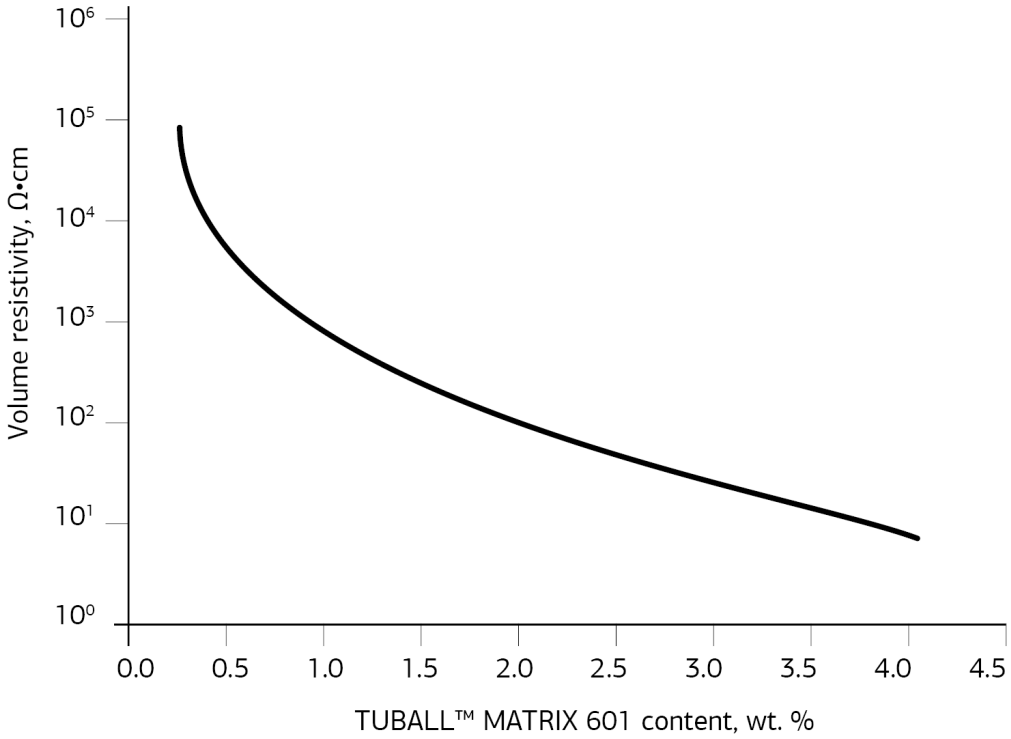



**Figure 3.** Volume resistivity of **RTV** with **TUBALL™ MATRIX 601** is in the range $10^5$–$10^1$ Ω·cm*

* Tested in two-component RTV (basic viscosity 25 000 mPa.s), dilution in part A. Measurements conducted according to ASTM D991 standard.

# High-speed mixer

For laboratory tests, a mechanical overhead stirrer with a mixing speed of up to 2000 rpm (4.2 m/s) (such as the Heidolph RZR series or the IKA EUROSTAR series).

Dilution should conducted in a cylindrical mixing container with a flat bottom. An example of an overhead stirrer is shown in Figure 4. The recommended impeller blade shape for maximum effectiveness is shown in Figure 5. This is relevant for the viscosity of a silicone-TUBALL™ system of not more than 250 000 mPa·s when the concentration of the TUBALL™ MATRIX is not more than 3%.

**! NOTE. 250 000 mPa·s is the maximum viscosity could be mixed on high speed mixer according to technical characteristics.**

**Figure 4.** Example of an overhead stirrer

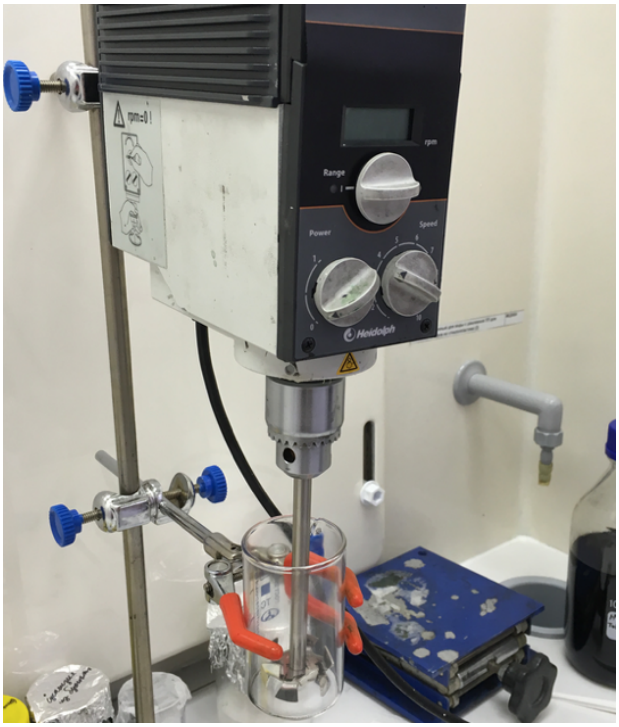
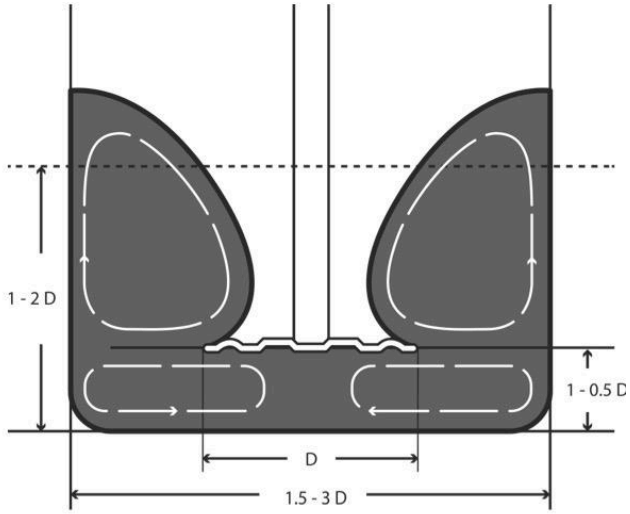


**Figure 5.** Recommended impeller blade shape

# PRINCIPLES

- The target dosage of TUBALL™ MATRIX refers to the loading in the whole final formulation.
- The temperature, time and mixing speed may need to be adapted to obtain a final mixture that is homogeneous.
- Increasing the rotation speed is a more effective way to obtain better dispersion quality than increasing the mixing time.
- During the dilution process, check the impeller blade and the walls and bottom of the container for stuck masses of TUBALL™ MATRIX.

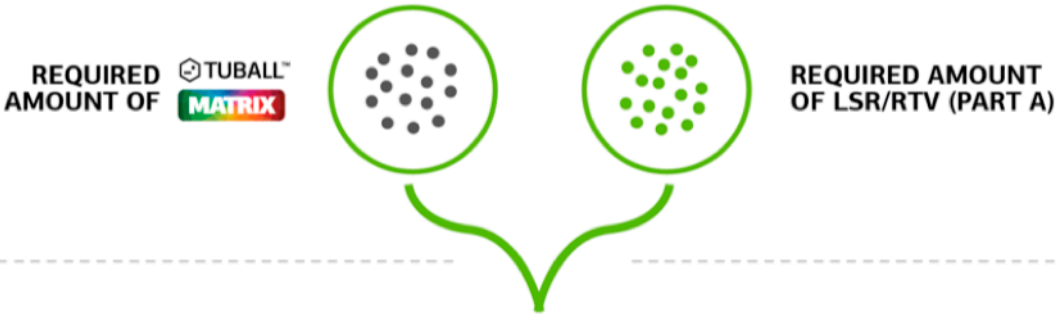
**Figure 6.** The optimal relative position of the stirrer, container and mixed volume.



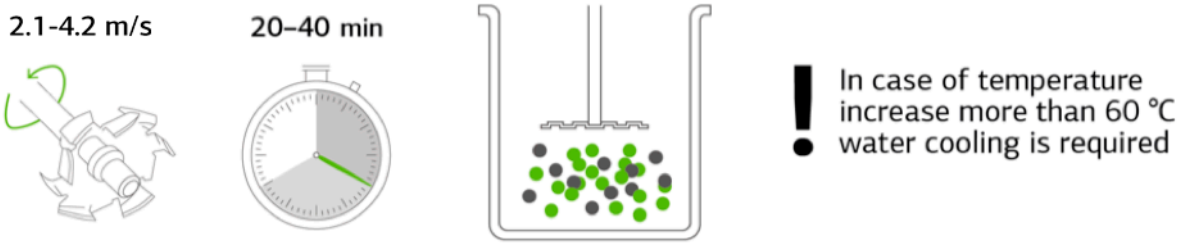

| Peripheral speed, 4,2 m/s | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| DIAMETER, mm | 50 | 100 | 150 | 200 | 250 | 300 | 350 | 400 | 450 | 500 |
| SHAFT SPEED, rpm | 1605 | 803 | 535 | 401 | 321 | 268 | 229 | 201 | 178 | 161 |

**TUBALL™ MATRIX (Direct mixing). Volume resistivity $10^3$–$10^{11}$ Ω·cm.**

Stage 1

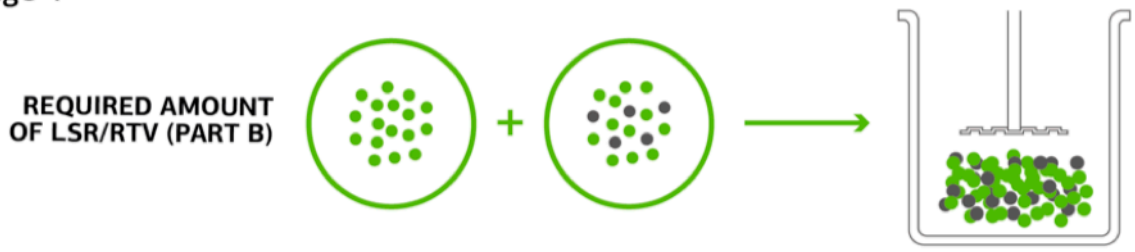



Stage 2




Stage 3


Stage 4




Stage 5

Deaerating procedure


Stage 6

Curing process according to normal procedure

# 3. DILUTION PROCEDURE IN HIGH VISCOUS SILICONES (>200 000 mPa·s)

## Three-roll mill

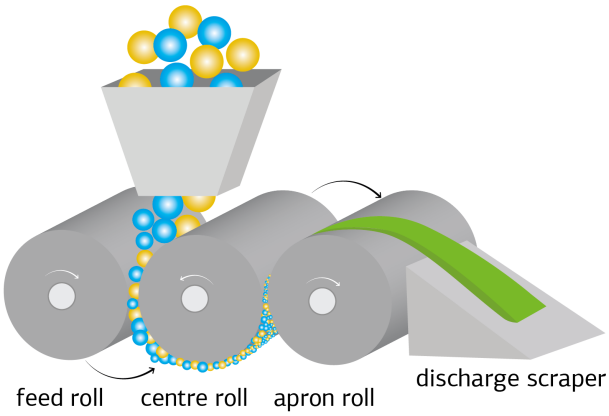
If the base material has higher viscosity (more than 200 000 mPa·s which is equal to more than 600 000 mPa·s with TUBALL™ MATRIX-silicone system), a three-roll mill (TRM) is required to dilute the **TUBALL™ MATRIX 601/602.**

A three-roll mill is a machine composed of three horizontally positioned rolls rotating in opposite directions and at different speeds. The rolls create shear forces to mix, refine, disperse and homogenise viscous materials.

An example of an Three-roll mill is shown in Figure 7, 8.

**Figure 7.** Example of a three-roll mill

**Figure 8.** Schematic diagram of the general configuration of a three-roll mill mechanism




**Dispersion on three-roll mill**

The following are general recommendations on three-roll mill operating parameters:

**Gap size between rolls.**

In terms of gap size regulation, there are two types of three-roll mill:

- **electronic** with precise gap control;
- **mechanical** with manual gap control.

For electronic mills, a gradual decrease in the gap size should be used as the most efficient way to disperse TUBALL™. For mechanical mills, a constant gap size should be set up at the beginning and retained throughout all milling cycles. Examples of recommended parameters for both types of mill are provided in the table below.

**Temperature control.**

It is recommended to use internal water cooling to maintain the rolls at the proper temperature, for the best reproducibility of results. Set the temperature to a constant value between 15 °C and 30 °C.

**Milling cycles.**
The number of cycles may vary depending on the type of three-roll mill and the carrier medium. Milling should be continued until the size of agglomerates decreases to a constant value or to a value suitable for your specific application. For an increased roll diameter, the number of milling cycles should be reduced. Excessive milling time increases the amount of damage to the nanotubes' structure, resulting in reduced conductivity.

**Hydraulic pressure.**
For advanced three-roll mills with the ability to operate in force mode, OCSiAl recommends that the linear pressure between the feed roll and the centre roll be set in the range of 3–5 N/cm and that between the centre and the apron roll be set in the range of 10–15 N/cm and to process for 7–10 cycles.

The parameters outlined in the table below are based on tests carried out by OCSiAl in 2016–2018, but it is recommended that preliminary tests always be carried out to optimize results.

A single milling cycle includes:
**A.** Loading material between the feed roll and the center roll;
**B.** Passing material through the gaps between the rolls;
**C.** Accumulating material on the knife edge after exiting the apron roll.

The table below contains recommended parameters for three-roll mill operation.
**Introduction of TUBALL™ MATRIX into part A and part B (separately).**

**Table 1.** Parameters of dispersion on three-roll mills.

| Model | Gap between rollers, μm | Number of cycles | Minimum batch, g | Maximum batch, g |
|---|---|---|---|---|
| Electronic mills (data for EXAKT 80 E) | 120/40 | 2 | 10 | 100 |
| Mechanical mills (data for SOWER S-150) | 20/10 | 2 | 100 | — |
| Mechanical mills (data for SOWER S-150) | 80/40 | 4 | — | 1000 |
| Mechanical mills (data for SOWER S-260) | 80/40 | 4 | 1000 | — |
| Mechanical mills (data for SOWER S-260) | 160/80 | 4 | — | 15000 |

After introduction of TUBALL™ MATRIX into Part A and Part B it could be mixed with static mixer (injection molding) under the normal conditions.

NOTE: Please do mention that distribution of TUBALL™ MATRIX in final compound depends on both stages – initial compounding stage (introduction into Part A and B) and injection molding (compounding of Part A and B). Normally, injection molding does not require any specific conditions with TUBALL™ MATRIX presence, but few options of initial compounding stage (introduction into Part A and B) could be tested in combination with normal injection molding regimes to achieve an optimal result.

**! Only in case of laboratory trials or compression molding compounding of part A and part B could be performed with Three-roll mil.**

| Model | Gap between rollers, μm | Number of cycles | Minimum batch, g | Maximum batch, g |
|---|---|---|---|---|
| Electronic mills (data for EXAKT 80 E) | 45/15 | 5 | 10 | 100 |
| Mechanical mills (data for SOWER S-150) | 20/10 | 7 | 100 | — |
| Mechanical mills (data for SOWER S-150) | 80/40 | 7 | — | 1000 |
| Mechanical mills (data for SOWER S-260) | 80/40 | 7 | 1000 | — |
| Mechanical mills (data for SOWER S-260) | 160/80 | 7 | — | 15000 |

# 4. EXAMPLES OF CALCULATIONS AND COMPOUNDING

**High speed mixer for two-component low viscosity silicone (< 50 000 mPa·s) compounds**

Desired level of conductivity is $10^2$ Ω·cm (3% **TUBALL™ MATRIX 601**)

- Composition of final compound (1 kg):
  48.5% of RTV component A — 485 g;
  48.5% of RTV component B — 485 g;
  3% of **TUBALL™ MATRIX 601** — 30 g.
- Mix 30 g of **TUBALL™ MATRIX 601** and 485 g of RTV component A.
- Mix at 2.1 – 4.2 m/s for 20–40 minutes at room temperature until a good dispersion quality is achieved.
- Add 485 g of RTV component B.
- Mix the system until it is homogeneous.
- Initiate the curing process according to the standard procedure.

**Three-roll mill for two-component high viscosity (under 200 000 mPa·s) silicone compounds or high MATRIX dosage compounds**

a) Volume resistivity $10^9$–$10^3$ Ω·cm
   Two-component silicone A:B (1:1)
   Desired level of resistivity below $10^2$ Ω·cm (3–5% **TUBALL™ MATRIX 601,** depending on the viscosity of silicone)

- Composition of final compound (1 kg):
  47.5% of component A — 475 g;
  47.5% of component B — 475 g;
  5% of **TUBALL™ MATRIX 601** — 50 g.
- Mix 25 g of **TUBALL™ MATRIX 601** and 475 g of component A using three-roll mill (dispersion 1).
- Mix 25 g of **TUBALL™ MATRIX 601** and 475 g of component B using three-roll mill (dispersion 2).
- Mix dispersion 1 and dispersion 2 using three-roll mill.

b) Two-component silicone A:B (9:1). Desired level of resistivity below $10^2$ Ω·cm (5% **TUBALL™ MATRIX 601**).

- Composition of final compound (1 kg):
  85.5% of RTV component A — 855 g;
  9.5% of RTV component B — 95 g;
  5% of **TUBALL™ MATRIX 601** — 50 g.
- Mix 50 g of **TUBALL™ MATRIX 601** and 855 g of RTV component A using three-roll mill (dispersion 1).
- Mix dispersion 1 and component B using three-roll mill.

The number of milling cycles and the spacing between shafts can changed and should be optimized for the specific materials.

Examples are given on the basis of OCSiAl experiments, exact concentration depends on the viscosity of basic material, parameters of equipment, etc.

**For an exact regimes for three-roll mill refer to Table 1 and 2 above.**

# 5. DISPERSION QUALITY CONTROL

## Visual control of the quality of MATRIX dispersion in silicone

This type of control is a visual test for the presence or absence of particles **TUBALL™ MATRIX** with a size of not more than 100–150 μm, in an amount not exceeding 15% of the total inclusions.

To carry out the test, select a small amount of the investigated dispersion and clamp it between two glasses of size 10×10 cm. The Figure 9, shows the type of poor dispersion (a) and good dispersion (b) when using a magnifier 15x.

a b

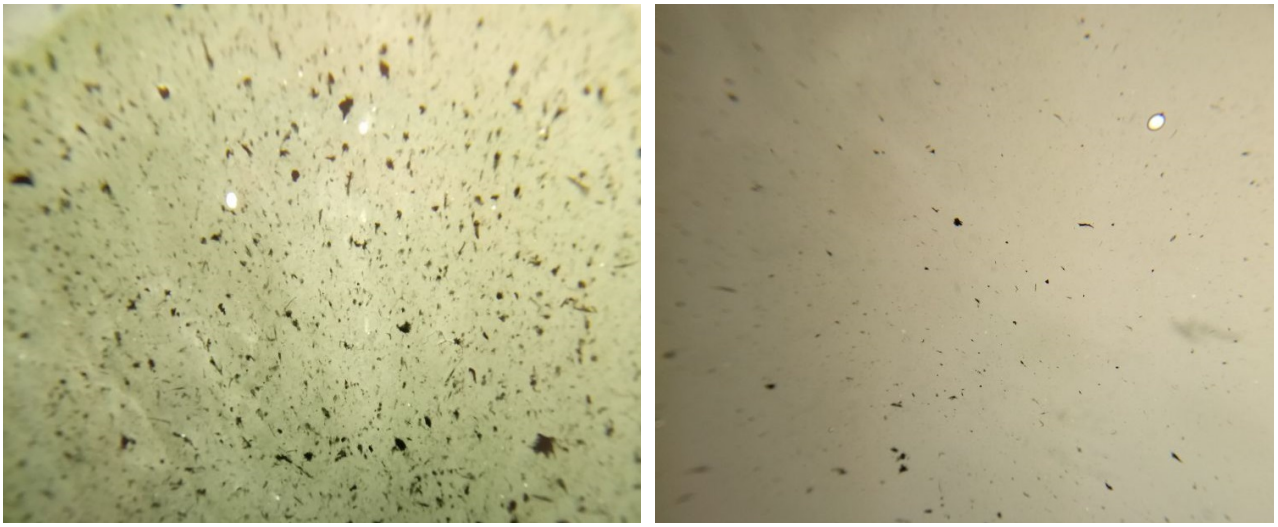


**Figure 9.** Examples of a visual test for determining the dispersion quality
Digital pocket microscope PO-9093 DPM 300 (BYK)

# Measurement of resistivity

For measurements of resistivity of uncured samples based on RTV or LSR, a hollow cylindrical cell with dimensions limited by electrodes with the same shape can be used. The resistance is measured with a multimeter connected to the electrodes. This method and equipment can be used when the target specific resistance value in the material is $10^8$ Ω·cm and lower. The voltage during the measurement should be 50 V.

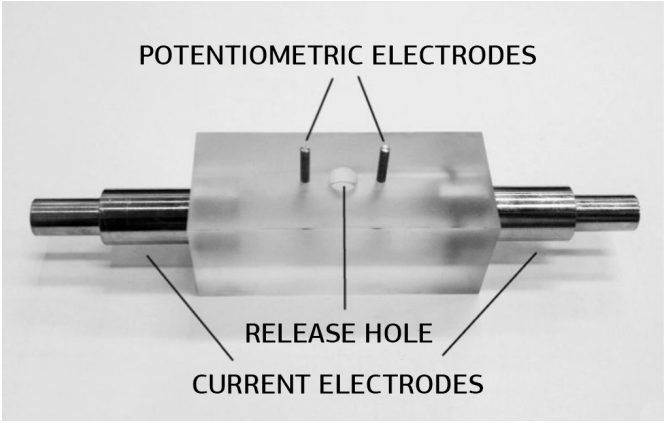
This technique is based on ISO 3915 "Plastics – Measurement of resistivity of conductive plastics" and adapted for conductivity measurement of paste-like substances. Based on a four-probe method, the principle is to measure a voltage drop on a certain dimensional part of a sample while putting a known current through it.

**Equipment**

- Benchtop laboratory mixer/dissolver;
- 100 ml beaker;
- Four-probe ohmic cell;
- Current source, 0–50 V, 0–3 A;
- DC voltmeter with inner resistivity of 10 MΩ (multimeter);
- DC ammeter from 10 μA (multimeter).

The recommended configuration of the ohmic cell for resistivity measurement is shown in Figure 10.

**Figure 10.** Ohmic cell for resistivity measurement




**Materials**

- Body: Plexiglas® (poly(methyl methacrylate));
- Potentiometric and current electrodes: stainless steel.

**Procedure**

The current electrodes act as plungers and are introduced from the opposite ends. The middle channel serves as a release hole to remove excess amounts of sample and air bubbles once the current electrodes are pushed in.

The potentiometric electrodes are inserted after the sample is loaded and the current electrodes are in the ready position.

**Connecting devices**

Connect all devices according to the diagram in Figure 11.

Pay attention to connect the ammeter in series between the current source and the ohmic cell.

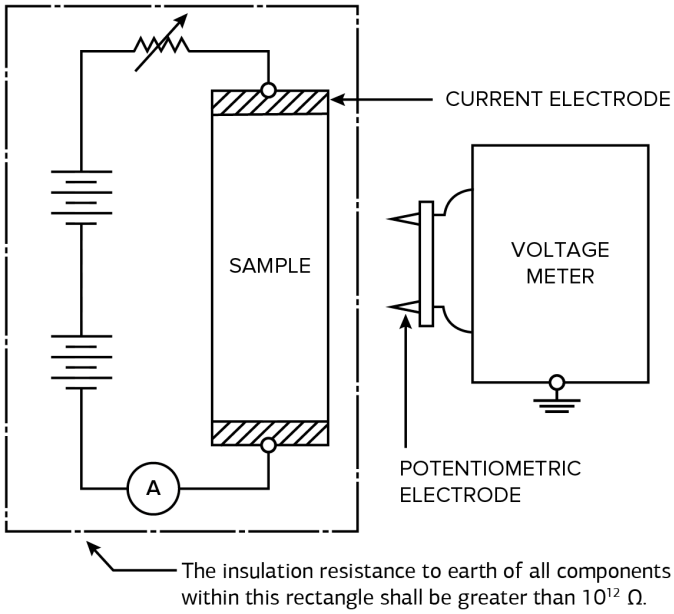



**Figure 11.** Diagram of the electric circuit

### Conducting measurements

After connecting all devices, switch the ammeter, voltmeter and current/voltage source ON, slowly apply a voltage up to 50 V, and set the corresponding range for current and voltage measurement.

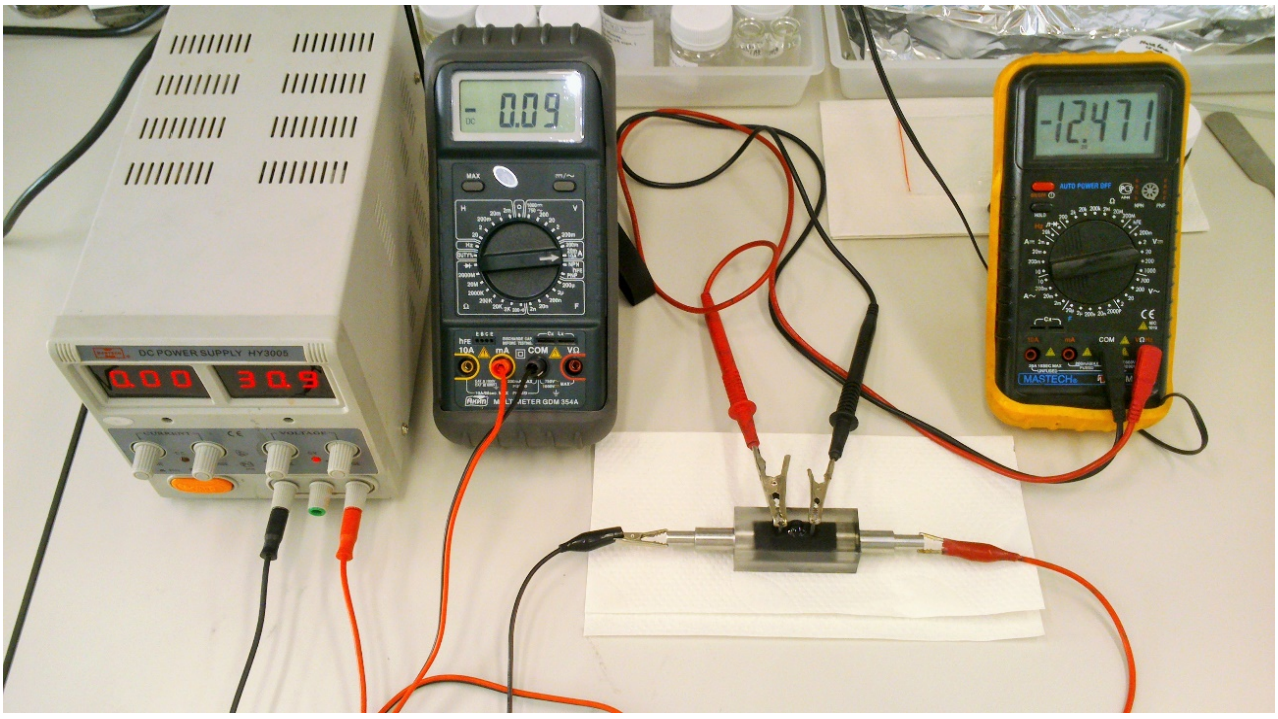



**Figure 12.** An example of a measurement set-up.

## Calculations

The resistance $R$, in ohms (Ω), is calculated according to the formula

$$R = \frac{\Delta U}{I} \qquad (1)$$

where

$\Delta U$ is the voltage drop, in volts (V), between the potentiometric electrodes;

$I$ is the current, in amperes (A), passing through the sample.

The volume resistivity $\rho$, in ohm-centimetres (Ω·cm), is calculated according to the formula

$$\rho = \frac{R \cdot S}{l} \qquad (2)$$

where

$R$ is the resistance, in ohms (Ω), calculated in (1);

$S$ is the cross-sectional area of the sample, perpendicular to the current flow, in $cm^2$;

$l$ is the distance between the potentiometric electrodes, in cm.

# 6. TROUBLESHOOTING

**Shelf life of compound**

The shelf life of the final compound in the uncured state must be determined experimentally for each particular compound. According to OCSiAl internal tests, liquid silicon rubbers compounded with TUBALL™ MATRIX 601/602 has stable electrical properties during 6-10 month.

**Impact to curing parameters**

TUBALL™ MATRIX 601/602 is compatible with platinum curing system. In case of high loading of TUBALL™ MATRIX (5 wt.% and more) is required to achieve low electrical resistivity compounds, some impact to curing system could happen. In this case, adjustment of curing system is required.

**Post curing**

Electrical conductivity is typically increased by the post curing process. For example, a volume resistivity of $10^8$ Ω·cm after curing will improve further down to $10^6$ Ω·cm after post curing for 4 hours at 200 °C. An exact impact depends on curing agents and moulding process.

**Moulding process**

Electrical conductivity could be affected by the moulding process due to differences in the shear forces. All the data provided in technical documents is based on a compression moulding process.

- Compression moulding — no impact on electrical conductivity.
- Injection moulding — resistivity is higher than with compression-moulded parts.

An exact impact to electrical resistivity by moulding process should be determined an experimental way.

**Impact to colour**

An example of compounding of colored samples by three-roll mill.

Two-component silicone A:B (1:1).

Desired level of resistivity $10^5$–$10^7$ Ω·cm (1–1,5% **TUBALL™ MATRIX 601,** depending on the viscosity of silicone)

- Composition of final compound (1 kg):
  46% of component A — 460 g;
  46% of component B — 460 g;
  1% of **TUBALL™ MATRIX 601** — 10 g;
  2% of white pigment (paste) — 20 g;
  5–10% of red (or other color) pigment (paste) — 50–100 g.
- Mix 5 g of **TUBALL™ MATRIX 601**, 10 g white paste, 25 g (if 5%) red paste and 460 g of component A using 4 cycles (dispersion 1).
- Mix 5 g of **TUBALL™ MATRIX 601**, 10 g white paste, 25 g (if 5%) red paste and 460 g of component B using 4 cycles (dispersion 2).
- Mix dispersion 1 and dispersion 2 using 5 cycles on a three-roll mill. Gap size is 80/40 μm.

**If the product is coloured**, then the number of cycles during final mixing should be optimised by considering the colour uniformity. For this, visual analysis is needed. For example, for the colour recipe shown below, it is evident that at least 7 cycles are needed to achieve the best colour uniformity.