Dipl.-Chem. Horst Müller, Dipl.-Ing. Ernstjürgen Klapp

MKU Carrier Fluids for the preparation of Slurries - Development and Tendency

Lecture on the occasion of the Silicon Conference 2008 in CZ Roznov

Slide 1:

In the semi-conductor industry and in many other application areas, wafers and similar sheet shaped work pieces are predominantly manufactured today by using the Wire-Saw Slicing Technology. In this operation, slurries are used. The efficiency of such a slurry depends strongly upon the carrier fluid used to prepare it.

Since more than 10 years MKU-Chemie developed and manufactures carrier fluids for the preparation of slurries.

Slide 2:

Who is MKU®-Chemie GmbH

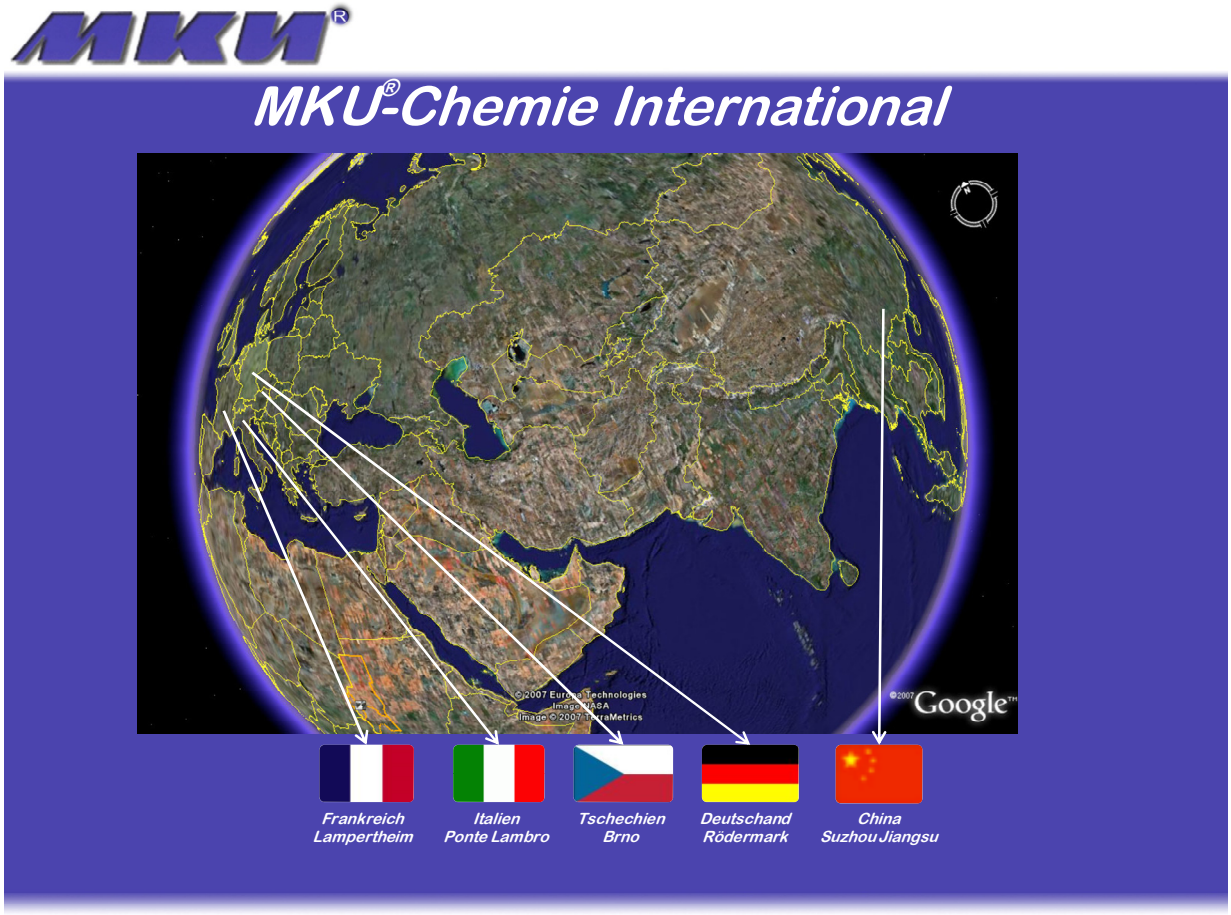
- MKU® supplies Metal-, Glass-, Ceramic-, Semiconductor-, Wood-, Plastic-, and Rubber Industry.
- MKU® produces water miscible and neat mineral oil and mineral oil free coolants and lubricants.
- MKU® produces hydraulic fluids, gear and circulation oils (according to DIN specifications), cleaners and release agents.
- MKU® is manufacturer for intermediate products (corrosion inhibitors, emulsifiers, AW- and EP-Additives).
- MKU® has an own development department for additives and finished Products as well as own manufacturing plants.
- MKU® has approximately 1.600 products, most of them (>90 %) are customer related specialties (tayloe made products).

Slide 3

Companies History

- 1956 – Founding of Mineralöl Klapp Urberach in the community of Urberach
- 1995 – Founding of MKU®-Chemie CZ in Brno (Czech Republic)
- 1996 – Founding of MKU®-Chimie S.a.r.l. in Lampertheim (France)
- 2005 – Affiliate office in China opened
- 2007 – Founding of MKU®-Chemie China
- 2008 – Founding of MKU®-Chemie Italy

Slide 4:



On the occasion of the Silicon Conference 2004, MKU reported here about "Technological Basics and Application Results of MKU Carrier Fluids used for Wire Sawing Operations in the Wafer Production."

Two years later on the Silicon Conference 2006, MKU informed about their activities in general and their products for wire slicing operations in particular.

The products introduced are manufactured from MKU-Chemie on the basis of balanced formulations using selected mineral oils and polyglycols, compounded with special additives. Slurries prepared with these carrier fluids are characterised by highest cutting rates (cm^2/min) and very low cutting forces (power consumption of the slicing unit)

Today, MKU wants to inform you about further developments on carrier fluid and cleaner technology that have been carried out during the last two years.

The permanent contact and co-operation with wafer manufacturers and Research institutes, enables MKU to adapt and continue their development works to the prevailing requirements.

As with all industrial manufacturing processes also wafer production is under great economical pressure. Permanently rising costs for raw materials, energy, wages etc. force to improved and more productive processes.

Among others, the wafer and photovoltaic industry is focused on an improved and increased yield of cut wafers. This led to the tendency to decrease the diameter of the wires, in order to achieve a higher yield from the silicon ingots.

This development requires an adaptation of the needed agents as carrier fluid, slurry, grain volume, and grain size, as well as their ratio in the used slurry.

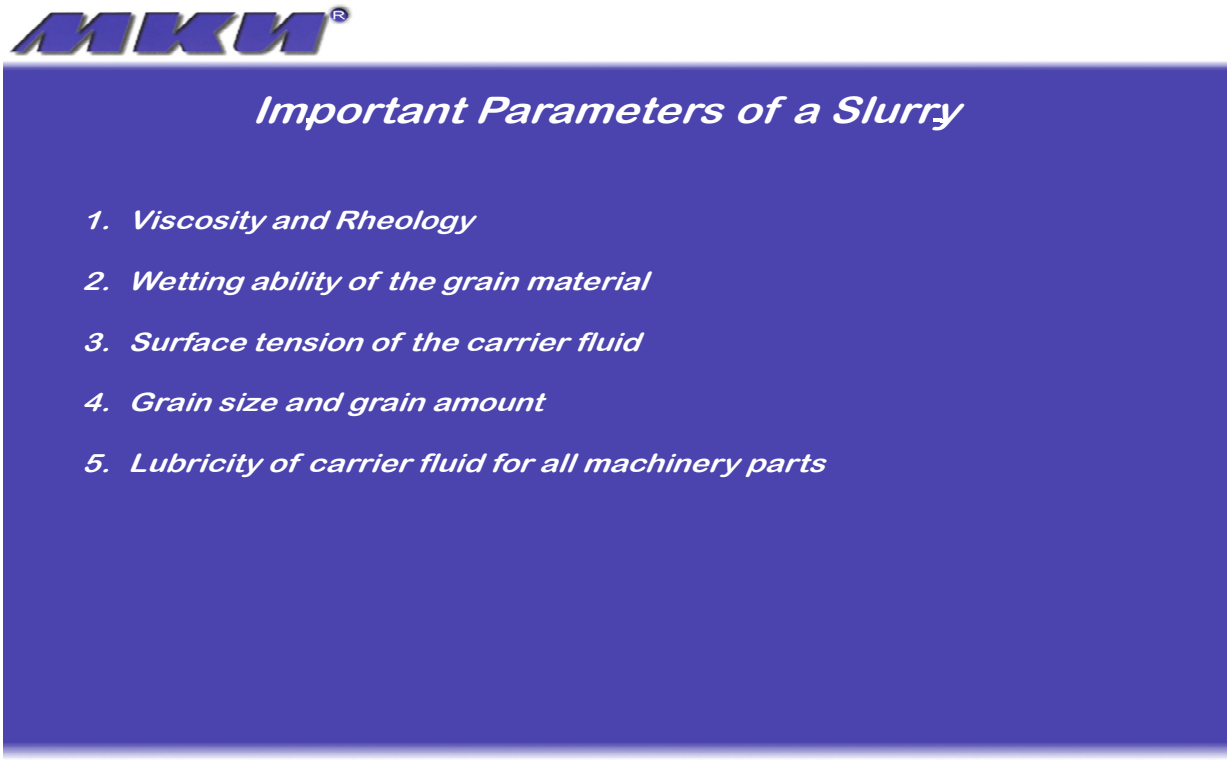
The needed slurry for wire slicing consists of a carrier fluid and a certain volume of finely distributed and suspended, abrasive grain material of a determined grain size and grain geometry.

The properties of a slurry as well as the combined effect with the wire tool and the basics of the slurry technology has been reported on the Silicon Conference 2004. When concentration of grain material is discussed, it is important to notice whether volume or mass concentration is concerned.

Carrier Fluids – Rheological Properties

A carrier fluid has the function to keep the added grains in an optimal suspension. This requires good dispersion properties of fluid and grains, at least for the time of the working process. Decisive characteristics for the efficiency of a carrier fluid are its physical properties, particularly the rheological properties.
Carrier fluids can consist of mineral oil or polyglycol. The characteristic to keep solid particulates in suspension depends upon several parameters.

Slide 5:



Together with the use of lower grain size (smaller grains) an adaptation of the carrier fluid properties is necessary. That is, the viscosity has to be lowered without decreasing the dispersion properties.

But, lower viscosity of the carrier fluid connected with the use of altered grain parameters, decrease the ability of the carrier fluid to keep the grains in suspension. This is valid for both fluids, mineral oil and polyglycol based. Furthermore, the carrier fluid loses lubricity with decreasing viscosity and causes an increase of friction of the wires at the cutting zone and the rollers. Simultaneously, the surface quality of the sliced wafers deteriorates, the specific cutting forces are increased along with an increase of temperature and increased wear of wires, resulting in higher energy consumption.

Considering these conditions, it can be stated that the properties of mineral oil based carrier fluids are superior to polyglycol-based fluids, because mineral oil of all viscosity grades can be adjusted to the corresponding requirements by adding of appropriate additives.

With polyglycols the possibilities of an adjustment with additives is limited, especially due to the missing compatibility with suitable additives.

Slide 6:

Comparison of Mineral Oil vs. Polyglycol

Properties	Mineral Oil	Dionol Extra V 1591-Qualities	PEG
Especially developed for wire sawing	no	yes	no
Dispersant Properties	good	excellent	poor
Service life of Slurry	good	good	sufficient
Viscosity/SiC concentration	high	low	sufficient
SiC cost per cut	sufficient	low	high
Lubricity	poor	excellent	insufficient
Friction in SiC film	acceptable	low	high
Cutting Temperature	acceptable	low	high
Thermal Stress in cut	acceptable	low	high
Energy consumption	acceptable	low	high
Water absorption	low	low	high
Change in Viscosity	low	low	high
Process stability	sufficient	excellent	sufficient

Source: Dr.-Ing. Rainer Godo, Dipl.-Ing. Ernstjürgen Klapp

Slide 7:

Comparison of Mineral Oil vs. Polyglycol

Properties	Mineral Oil	Dionol Extra V 1591-Qualities	PEG
Quality of Cut	good	excellent	acceptable
Corrosion	no	no	high
Service life wire guides	sufficient	high	short
Service life pulleys	sufficient	high	short
Advantage with thin wire	yes	yes	no
Adhesive removing	good	good	good
Handling	simple	simple	simple
Safety	safe	safe	safe
Disposal	combustion	combustion	recycling possible
Cost	low	high	low
Cost efficiency	good	excellent	acceptable

Source: Dr.-Ing. Rainer Godo, Dipl.-Ing. Ernstjürgen Klapp

Which parameters have an influence on the performance of a slurry?

1. Viscosity

Carrier fluids, both mineral oil or polyglycol based, are Newtonian Fluids, while the slurries of both as solid-liquid mixture have no more Newtonian properties. Nevertheless, the carrier fluids follow the Newtonian law and remain their viscosity – temperature behaviour without consideration to the solid part, also when blended with solid particulates.

As already mentioned, the viscosity of mineral oils can be adjusted easier than the viscosity of polyglycols. The lowest viscosity of polyglycol is those of PEG 200 that is limited with 53-62 mm^2/s at 20°C or 20-26 mm^2/s at 40°C respectively, depending upon the molecular mass distribution.

Low molecular polyglycols are water soluble and have the ability to absorb water to a great extend. This property is often used to dilute the carrier fluid for economical reasons. The water absorption however, has the consequence of a significant decrease in viscosity, followed by decreasing important properties, as wettability, lubricity, and corrosion protection. Additionally, micro-organisms contained in the added water can cause bacteriological attack and foulness of the fluid.

In comparison to polyglycols, mineral oils can be easily adjusted to higher or lower viscosities (lower than 10 mm^2/s at 40°C). Properties that have been changed by altered viscosity can be adjusted by adding appropriate additives.

Such low viscosity fluids allow the user to adjust the slurry itself in case of thickening of the slurry by contamination or low temperatures in winter time, or in case that a lower viscosity is needed for another operation.
Since carrier fluids of low viscosity are also formulated with the corresponding additives, there is no change of the other parameters when added to the fluid in use.

It is valid for all carrier fluids that with lower viscosity the ability to carry solid particulates decreases. As long as the slurry is in motion solid particulates are kept in motion and the tendency to separate is limited. As soon as the fluid comes to a resting point, the speed of particle separation increases suddenly. The lower the viscosity of the carrier fluid and the coarser the grit, the faster the separation. This is valid for both, polar and non-polar fluids.

2. Specific Gravity

The specific gravity of a carrier fluid has only little influence on the ability to keep particulates in suspension. Because of the higher specific gravity of polyglycols in comparison to mineral oil, there is a small noticeable difference.

The specific gravity for polyethylene glycols PEG 200 – PEG 600 ranges between 1.12 – 1.14 g/cm^3 at 15°C, depending upon the molecular mass distribution.

For mineral oils the specific gravity ranges between 0.85 and 0.89 g/cm^3, depending upon structure and viscosity.

Slide 8: Comparison of Viscosity vs. Specific Gravity and Lubricity

Product	Specific Gravity 15°C g/cm³	Viscosity at 40°C mm²/s	Lubricity N/cm²
Polyethylene glycol based			
PEG 300	1.13	30-40	1800
PEG 200	1.12	22-26	1600
Betronol® MF V 1016	1.13	30	2800
Betronol® MF V 1016-1	1.12	22	2000
Betronol® MF V 1016-2	1.08	23	1500
Betronol® MF V 1016-3	1.12	22	2000
Betronol® MF V 1016-4	1.12	28	1700
Betronol® MF V 1016-5	1.06	16	1550
Betronol® MF V 1016-6	1.04	14	1800
Betronol® MF V 1016-7	1.13	24	1800
Betronol® MF V 1016-8	1.08	26	1400
Mineral Oil			
Dionol® Extra V 1591	0.88	25	3600
Dionol® Extra V 1591-1	0.87	22	3600
Dionol® Extra V 1591-2	0.88	25	3600
Dionol® Extra V 1591-3	0.86	14	3600
Dionol® Extra V 1591-4	0.85	9	3600
Dionol® Extra V 1591-5	0.87	20	3600
Dionol® Extra V 1591-6	0.85	15	3100
Dionol® Extra V 1591-7	0.87	20	2800
Dionol® Extra V 1591-8	0.85	18	4500
Dionol® Extra V 1591-9	0.85	8-12	4500

From the figures of slide 7 the following conclusion can be stated:

1. The lubricity performance of slurries that are based on mineral oil is superior to those of PEG.

2. The viscosity of carrier fluids based on mineral oil can be lowered without deterioration of lubricity.

3. Polyglycols are limited in adjustment of viscosity, lubricity cannot essentially be improved.

3. Wettability

The wettability of a fluid depends, amongst other properties, upon its polarity to other materials.

Mineral oils are basically non-polar and have no surface active properties.

Polyglycols have a slightly different behaviour in polarity than mineral oils, but they also do not belong to surface active substances. Therefore, polyglycols have no significant advantage in comparison to mineral oils in suspending solid materials. An important property to suspend particulates in a fluid, is the wettability of the solid material.

As non-polar fluids, mineral oils have basically no wetting properties. This can be effectively changed by the addition of suitable additives with polar function.

Polyglycols have only a limited polarity, based on the oxygen- and hydroxyl-groups, but they cannot be adjusted to higher polarity to the same extend than mineral oils, just because of their functional groups.

4. Surface Tension

The surface tension of a fluid is in a direct relation to the polarity of a fluid and thus also to the wettability. Surface tension can also be altered by the addition of suitable additives.

The surface tension of polyethylene glycol with molar mass of 200-600 is approximately 40 dyn/cm^2.

The surface tension for mineral oils without additives is similar to those of polyethylene glycols, dependent upon the viscosity.

The following slide shows the surface tension of different carrier fluids versus their viscosities.

From this comparison it becomes obvious that carrier fluids based on mineral oil show essentially better values than polyglycols.

Slide 9:

Data of Surface Tension vs. Viscosity of MKU-Carrier Fluids

Product	Viscosity at 40°C mm²/s	Surface Tension dyn/cm²
Polyethylene glycol based		
PEG 200	22-26	37,5
PEG 300	30-40	43
Betronol® MF V 1016	30	39,5
Betronol® MF V 1016-2	23	43
Betronol® MF V 1016-5	16	33
Betronol® MF V 1016-6	14	33
Betronol® MF V 1016-7	24	33,5
Betronol® MF V 1016-8	26 (contains water)	49,5
Mineral Oil		
Mineral Oil A	100	32
Mineral Oil B	4,5	29
Dionol® Extra V 1591-2	25	30
Dionol® Extra V 1591-4	9	29,5
Dionol® Extra V 1591-9	8-12	29
Dionol® Extra V 1591-10	10	29

5. Grain Size and Shape of Grains

It is evident that smaller particulates can be better dispersed and kept in suspension than coarser ones.

Also the shape of particulates is of importance. Smooth particulates show less affinity to the carrier fluid than rough ones and have therefore, a higher tendency to separate and a higher speed of sedimentation.

MKU®-Chemie altered in some of their carrier fluids the rheological properties and the structure. By this measurement the suspending property of the fluid is essentially improved, the grains are better dispersed and the slurry shows better stability.

This development was done with selected polyglycols as well as with mineral oil based carrier fluids.

Due to the altered rheology and structure of he carrier fluids, the quantitative proportion between carrier fluid and grit, that is often used in practice in a ratio of 1:1, could be reduced to a ratio of 1:3. This means an economical saving of about 50 % of grit.

Further tests were carried out with smaller grain size. These tests showed, that caused by the greater surface of finer grains further savings could be possible but the test series are not yet finished and reliable results are currently still not available.

6. Speed of Sedimentation of Particulates in Slurries with different Carrier Fluids

Slide 10 and 11 show the sedimentation behaviour of particles of same kind and same concentration in different carrier fluids.

The test series have been carried out with a fluid volume of 250 cm^3 of each carrier fluid. To each carrier fluid sample the same amount (10%) of grains (F 400) was added and homogeneously dispersed.
After that, the speed of the grit-sedimentation in the test samples was measured every 25 minutes, and the result plotted into the graphics.

A measuring time of 42 hours led to the following result:

6.1. Speed of sedimentation in Polyglycol based Fluids

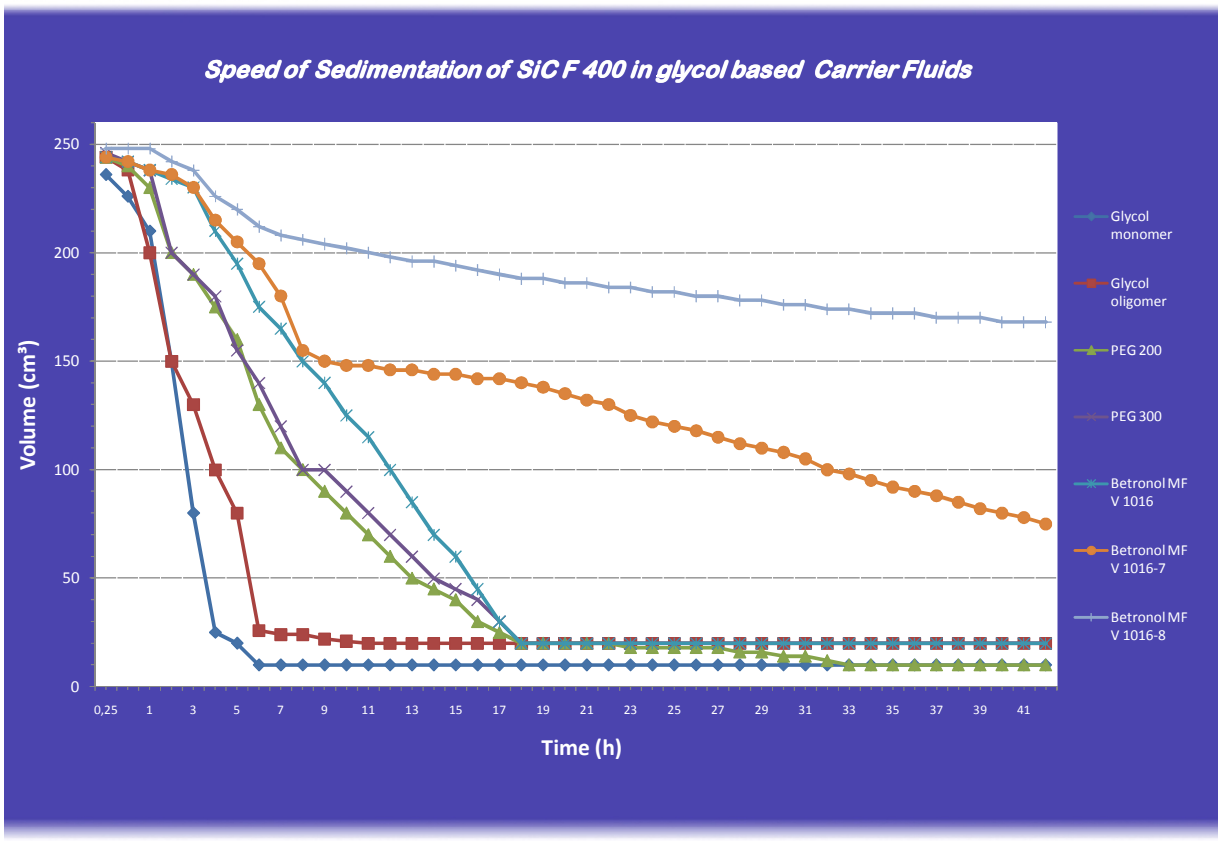
Four of the glycol-based fluids are without additives, in order to demonstrate the dependence of the sedimentation speed from the viscosity.

The sedimentation time for very low-viscous glycols was already ended after 6 hours, while the sedimentation time for the higher-viscous fluids PEG 200 and PEG 300 was three times as long and nearly equal for both of them.

Betronol® MF V 1016 is compounded with usual additives and the viscosity is similar to PEG 300. The speed of sedimentation was somewhat decelerated but ended similar as PEG 300 did.

A totally different picture show the results for Betronol® MFV 1016-7 and Betronol® MF V 1016-8.
Both products consists of rheologically structure altered carrier fluids, with the result that the speed of particle sedimentation is strongly decelerated and the time of separation is enormously improved.

Folie 10:



6.2. Speed of Sedimentation I Mineral Oil based Fluids

The results of these test series showed the same tendency of sedimentation as the tests with PEG-based fluids, but with a result to a much clearer extend.

The very low-viscous mineral oil B with a viscosity of 4,5 mm²/s at 40°C contains no additive. This oil has no ability to carry grains.

Quite good results for the speed of sedimentation have been obtained with mineral oil A, but the separation time ended abrupt after 18 hours, similar to that of PEG 300. With the very high viscosity of 100 cm²/s at 40°C, this oil is not suitable for use as carrier fluid.

Dionol® Extra V 1591-2 has a viscosity of 25 mm²/s at 40°C and is compounded with additives to lower friction and to improve lubricity in order to obtain better cutting results.
The speed of sedimentation shows for this fluid only a slight increase and a relatively short separation time.

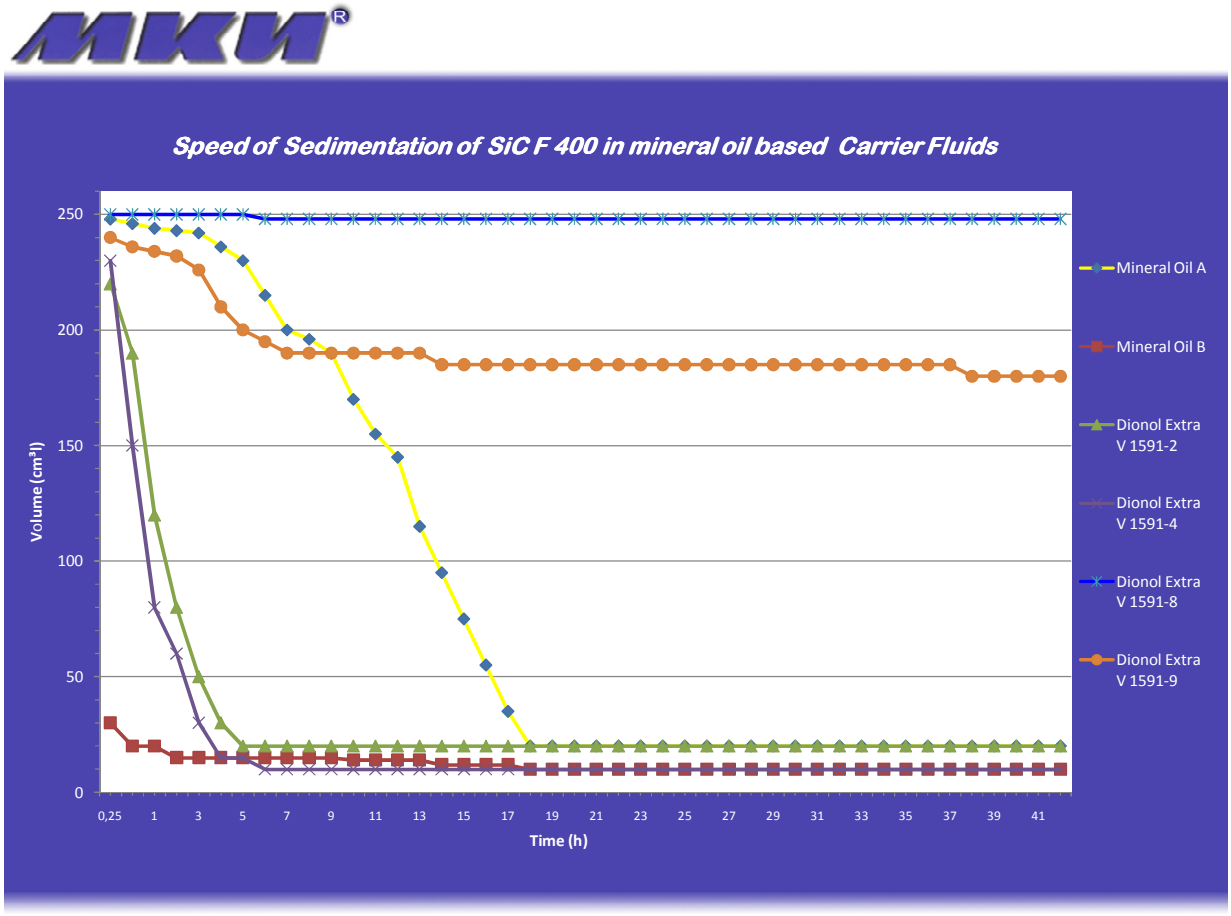
Dionol® Extra V 1591-4 is a very low viscous fluid with only 9 mm²/s at 40°C.
It contains additives to lower friction and to improve lubricity for better cutting results. This fluid is predominantly used as adjusting fluid for slurries that have been thickened by the time. The ability for grain suspension cannot be expected because of the very low viscosity.

Totally different is the behaviour of Dionol® Extra V 1591-8 and Dionol® Extra V 1591-9 which are rheologically structure altered by using nanotechnology.

Both fluids, but especially Dionol® Extra V 1591-8, show also after 42 hours a very high stability of the slurry and no tendency to separate. This is a tremendous advantage, also with regard to resting times of the machinery.
An economical separation of grains from these fluids is only possible with the use of mechanical processes.

MKU®-Chemie continues their efforts in further developments and will report theresults on the occasion of the next Silicon Conference in the year 2010.

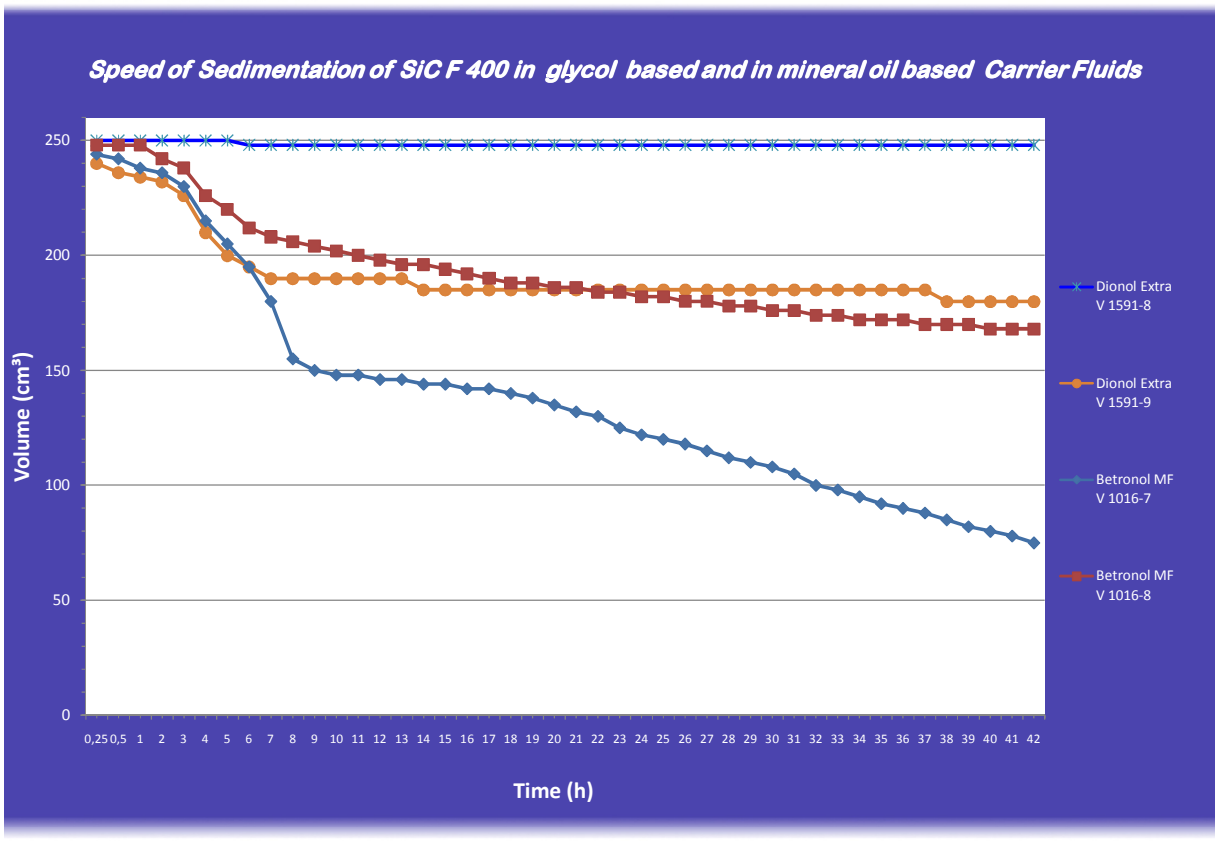
Folie 11:



6.3. Conclusion

The rheological behaviour of mineral oil-based carrier fluids can be easier and better affected than those of polyglycols. That means, by altering the rheological structure of a carrier fluid it is possible to use fluids with lower viscosity and evenimproved separation behaviour. Due to these property the amount of grains may be lowered.

Folie 12:



7. Recycling

Recycling of slurries is so far difficult as the used grit became worthless for further use, as a result of shape deformation (rounding) and contamination by silicon.

There are economical processes for the recycling of polyglycols. During usage polyglycols are exposed to aging (oxidation). Therefore, recycled polyglycol cannot be used without the addition of a certain amount of fresh polyglycol.

Mineral oil is also exposed to an aging process. Before reusing of for the preparation of new slurry, the grit has to be separated by sedimentation from the slurry, mineral oil must be decanted and then can be reused to prepare a new slurry, after addition of 60-70% of fresh oil.

Rheologically and structure altered carrier fluids have in fact a strongly extended ability for grit suspension, but just this property reduces the time of separation, and a sedimentation process can scarcely carried out in a sufficient time. Separation is only possible by using mechanical processes.

8. Description of MKU® - Product Series for Wire Slicing Operations

Slide 13:

Betronol® MF

- *Synthetic Carrier Fluids (Glycols) for the preparation of Slurries for Wire-Sawing Operations of Semiconductor Materials*

Dionol® Extra

- *Carrier Fluids (Mineral Oil) for the preparation of Slurries used for Wire-Sawing of Semiconductors Materials*

The individual carrier fluids are distinguished by their formulations corresponding to the different process parameters as e.g. grain size, grit proportion, speed of wire, diameter of wire and diameter of ingot.

MKU carrier fluids, developed on the basis of intensive research and practical slicing tests, are divided into the following two product series:

Dionol® - Series: Dionol® Extra V 1591-1 to 1591-15

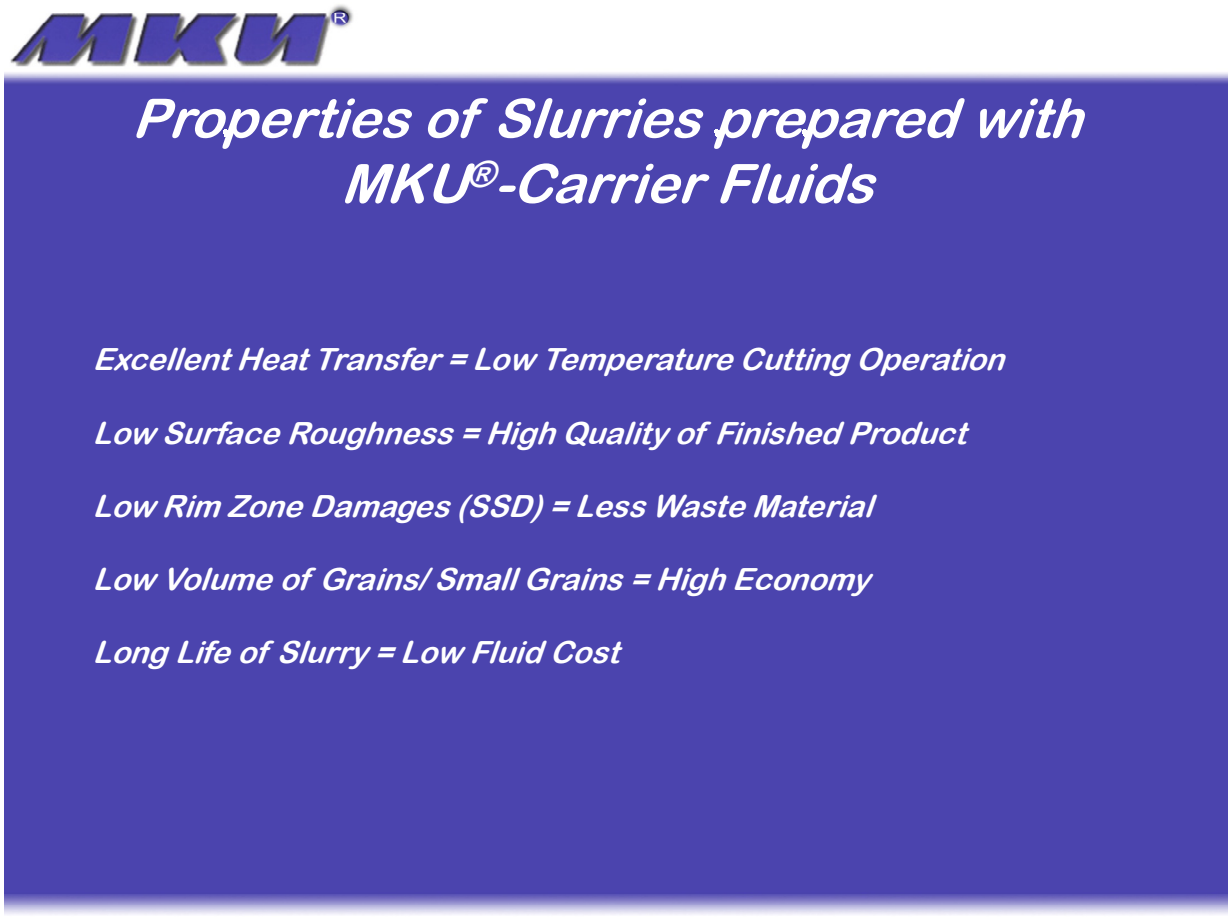
These fluids are based on differently formulated mineral oils that are compounded with additives, corresponding to their applications.
The slurries prepared with these fluids are characterised by high dispersant properties, sharp cuts (grip), and low friction losses.

Betronol®- Series: Betronol® MF V 1016-1 to 1016-15

These carrier fluids are based on special selected polyglycols and are particularly used in the photovoltaic industry. They are characterised by good dispersion properties, high slicing ratios, best surface qualities and optimal recycling properties.

Besides of a significant reduced energy consumption (30 % and more) the fluids of both product series are also characterised by high chemical stability and very good controlling of the assigned machinery type slicing process.

Slide 14:



Connected to the last point it is particularly important that slurries prepared with MKU® Fluids show no tendency to form hard sediment conglomerates, even not after long resting periods.

9. Tendency of Development

MKU®-Chemie works continuously on developments for further improvements of the carrier fluids, with the inclusion of modern nanotechnology in order to increase and combine the performance of both, carrier media – mineral oil and polyglycol – and to achieve further economical advantages in the production of wafers.

10. Cleaners for Wire Sliced Sheets

In connection with the carrier fluids, MKU® developed also novel water-soluble cleaners. For effective cleaning, alkaline and neutral cleaners are available as well.

Both, Alkolox and Neutralox cleaners remove residues of slurry, adhering on work pieces (also mineral oil based slurries) with highest efficiency and best surface quality. Carrier fluids and cleaners are optimal adjusted to each other and complement one another.

After slicing the sheets (e.g. silicon wafers) by means of wire-saw slicing process, the work pieces adhere very tight to each other and are wetted and contaminated with slurry. In order to make the separation and cleaning of the wafers to a simple following process, MKU® developed special cleaners that achieve best results, especially with slurries based on mineral oil. The attainable total cleaning and degreasing is based on an optimal chemical adaptation of the cleaners to the MKU® carrier fluids.

Slide 15:

Alkalox 580

This novel, water-soluble alkaline cleaner concentrate allows a perfect cleaning of wafers.
Alkalox 580 does not contain any organic solvent and the aqueous solutions are only less foaming. It is used to remove all types of contaminations and residues on work piece surfaces.

Diesel fuel is often used for pre-cleaning of semi-conductor wafers, which have been cut with mineral oil based slurries.
As a replacement for Diesel fuel, MKU® developed for this purpose a special flushing oil, Dionol® V 1685 that is not inflammable and not carcinogenic, as well as it is not subjected to VOC regulation.
The subsequent basic cleaning operation can be carried out with Alkalox 580 in a dilution with 50 % water at a cleansing temperature between 70°C and 75°C.

For wafers, cut with a polygylcol-based slurry, the above mentioned pre-, and basic cleaning operation becomes no longer necessary.

Ultrasonic cleaning operations of wafers, produced with mineral oil or polyglycol slurry, is carried out with a concentration of 10% to 15% Alkalox 580, at 70°C to 75°C, followed by rinsing with distilled water at 25°C, three to four times repeated.

For the final cleaning of the wafers a concentration of 2% to 5% is sufficient at 25°C. After the cleaning operation, Alkalox 580 can be rinsed off with distilled water at 25°C.

Neutralox 590

Neutralox 590 is a special, water-soluble neutral cleaner with low foaming tendency, and is free of organic solvents.

Neutralox removes all kind of contamination and residues from metal or ceramic work piece surfaces. It is used when increased surface quality of the work pieces is required.
Neutralox is one of the most effective cleaners for semi-conductor wafers.

In ultrasonic cleaning operations Neutralox 590 is added to the Alkalox 580 cleaner solution in a concentration of 0.5 % to 0 3% to obtain an improved cleaning result.

Summary

There are two cleaning operations less needed when using PEG slurries, but this has no influence on the cot of single cut.

Slide 16:

11. References

1. Application Results in Wire-Saw Slicing of Silicon Wafers based on the use of MKU® Carrier Fluid Technology.
   Günter Werner, Ernst Klapp/MKU®-Chemie GmbH Rödermark
   Silicon Conference 2004 in Roznov

2. Application Results in Wire-Saw Slicing of Silicon Wafers based on the use of MKU®-Carrier Fluids continued
   H.Müller, E. Klapp, MKU®-Chemie GmbH Rödermark
   Silicon Conference 2006 in Roznov