FRICTION, WEAR AND LUBRICATION

MEMM 1343

LUBRICANTS

Lubricants and their market

In 2007, a total of 37.2 million tons of lubricants was consumed worldwide (56% automotive oils, 35% industrial lubricants, including related specialties, and 9% process oils).

Among the total industrial lubricants, 37% were hydraulic oils, 7% industrial gear oils, 31% other industrial oils, 16% metalworking fluids (including temporary corrosion preventives, the multipurpose function of which often includes lubrication), and 9% greases. The segmental and regional breakdowns of the global lubricant market are shown on Figure 1 and Table 1.

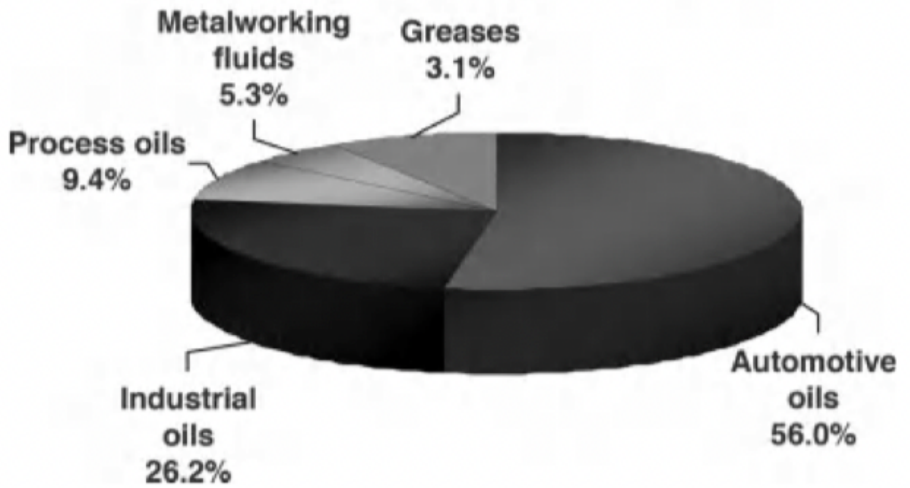
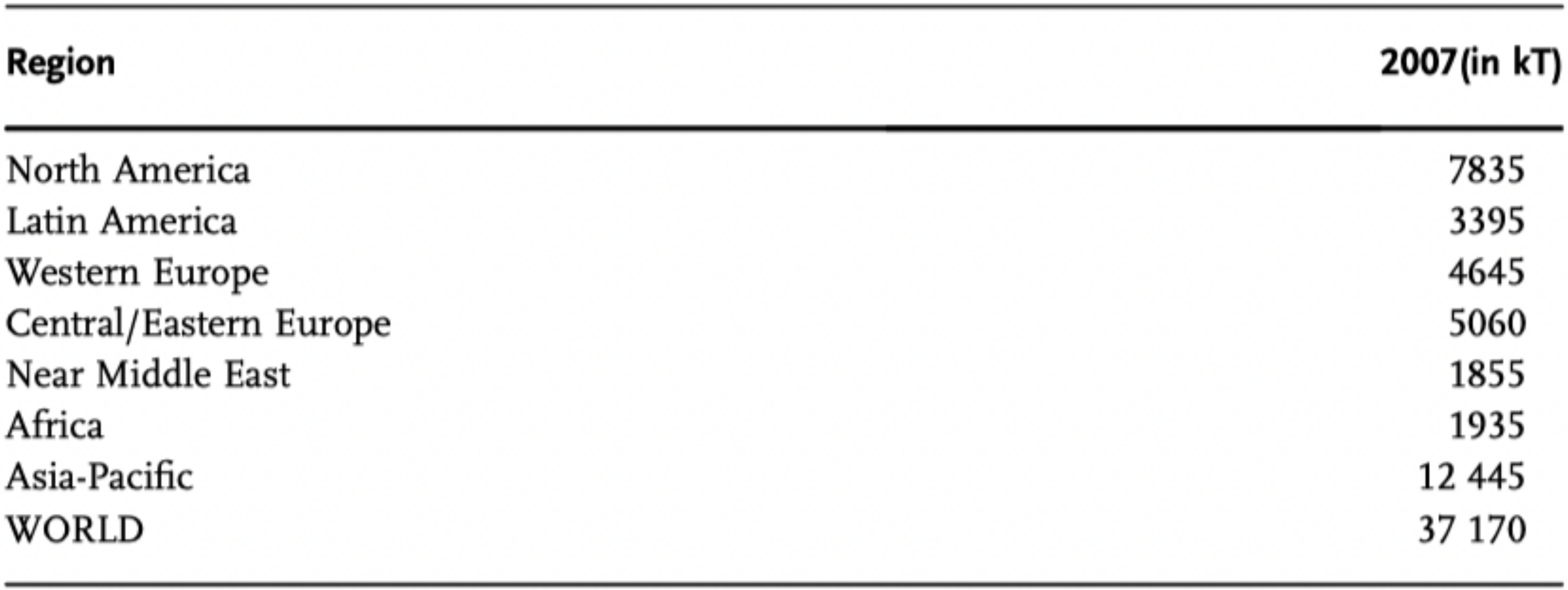


Figure 1: Segment break down of the global lubricant market in 2007

Table 1: Regional development of the global lubricant market.



Region	**2007(in kT)**
North America	7835
Latin America	3395
Western Europe	4645
Central/Eastern Europe	5060
Near Middle East	1855
Africa	1935
Asia-Pacific	12 445
WORLD	37 170

Details of the world's largest manufacturers of finished lubricants are listed in Figure 3.

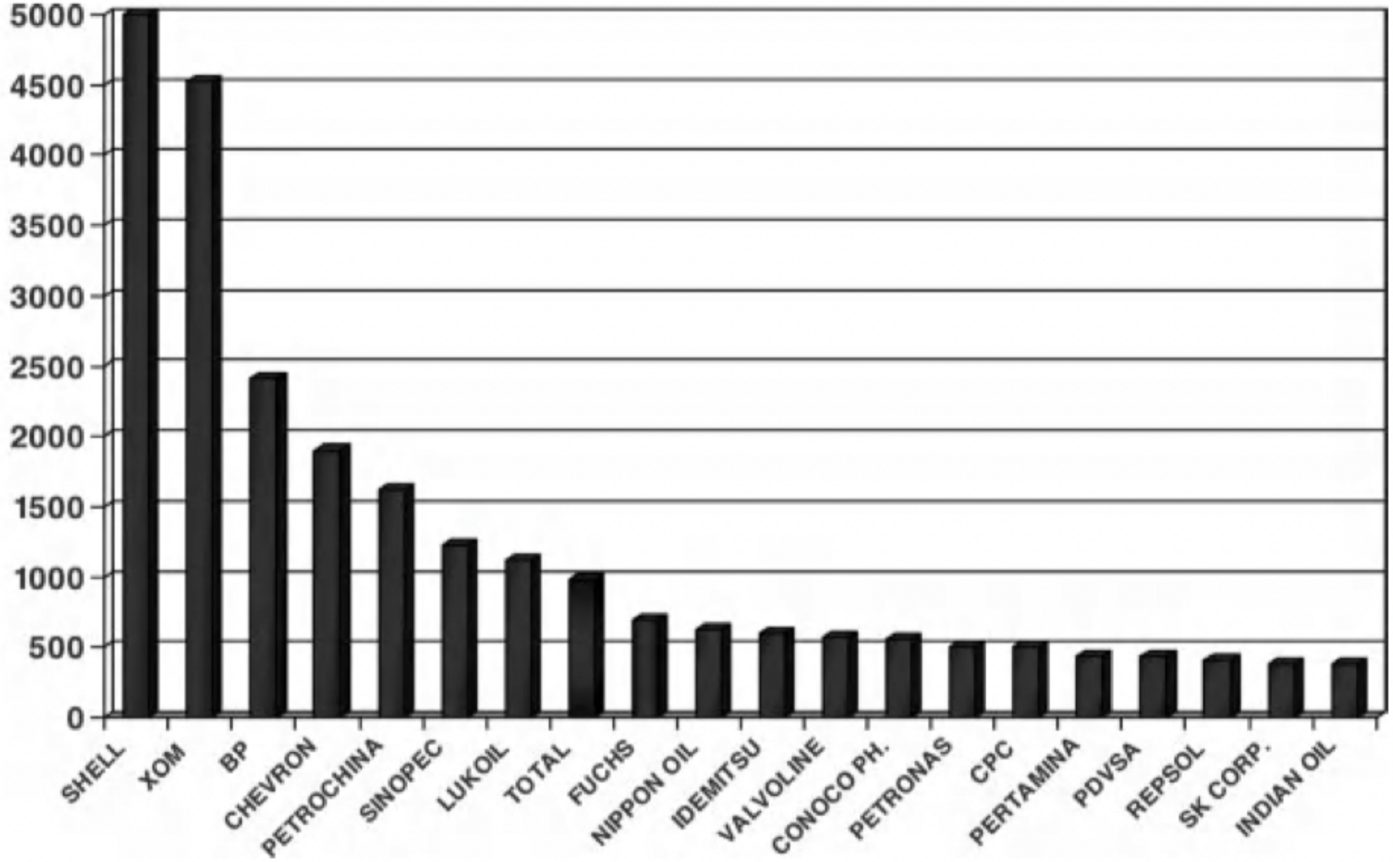


Figure 3: World ranking of the largest manufacturers of lubricants in 2007 (ktonnes per year)

PHYSICAL PROPERTIES OF LUBRICANTS

In simple terms, the function of a lubricant is to control friction and wear in a given system. The basic requirements therefore relate to the performance of the lubricant, i.e., its influence upon friction and wear characteristics of a system.

Another important aspect is the lubricant quality, which reflects its resistance to degradation in service. Most of the present day lubricant research is dedicated to the study, prevention and monitoring of oil degradation, since the lifetime of an oil is as important as its initial level of performance.

Apart from suffering degradation in service, which may cause damage to the operating machinery, an oil may cause corrosion of contacting surfaces. The oil quality, however, is not the only consideration. Economic considerations are also important. For example, in large machinery holding several thousand litres of lubricating oil, the cost of the oil can be very high.

Here, the fundamental physical properties of lubricants such as viscosity, viscosity temperature dependence, viscosity index, pour point, flash point, volatility, oxidation stability, thermal stability, etc., together with the appropriate units and the ways of measuring these values will be outlined.

Oil viscosity

The parameter that plays a fundamental role in lubrication is oil viscosity. Different oils exhibit different viscosities.

In addition, oil viscosity changes with temperature, shear rate and pressure and the thickness of the generated oil film is usually proportional to it. So, at first glance, it appears that the more viscous oils would give better performance, since the generated films would be thicker and a better separation of the two surfaces in contact would be achieved.

This unfortunately is not always the case since more viscous oils require more power to be sheared. Consequently the power losses are higher and more heat is generated resulting in a substantial increase in the temperature of the contacting surfaces, which may lead to the failure of the component.

For engineering applications the oil viscosity is usually chosen to give optimum performance at the required temperature. Knowing the temperature at which the oil is expected to operate is critical as oil viscosity is extremely temperature dependent.

The viscosity of different oils varies at different rates with temperature. It can also be affected by the velocities of the operating surfaces (shear rates). The knowledge of the viscosity characteristics of a lubricant is therefore important in the design and in the prediction of the behavior of a lubricated mechanical system.

Dynamic viscosity

To resist the applied force, P , a shearing stress, τ, would be developed at the plate-material interface, as shown in Figure 4. The equilibrium is;

$$P = \tau A$$

It revealed that we need more P (to move the plate) as the shearing stress, τ, is increased.

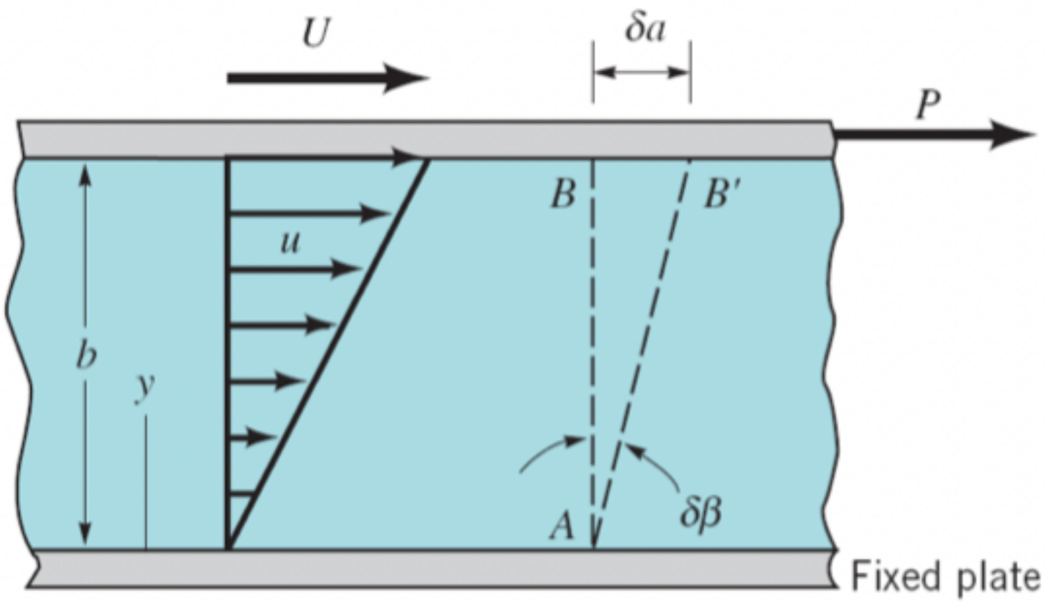


Figure 4: Schematic representation of the fluid separating two surfaces.

We can say that shear stress, τ, has direct proportion with the velocity gradient – that is ;

$$\tau \propto \frac{du}{dy}$$

The shearing stress and velocity gradient can be related with a relationship of the form ;

$$\tau = \mu \frac{du}{dy}$$

μ (miu) is a dynamic viscosity. Dynamic viscosity also called as an absolute viscosity.

Unit is kg/m.s or N.s/m^2 or Pa.s or Poise (P) or centipoise (cP)

1 Pa.s = 10 Poise

Kinematic viscosity

Kinematic viscosity is defined as the ratio of dynamic viscosity to fluid density.

Relation between dynamic viscosity and kinematic viscosity can be written as ; (ρ (rho) is the fluid density)

$$\mu = \rho \cdot \upsilon$$

υ (nu) is a kinematic viscosity. Unit is m^2/s or Stokes (St) or centiStokes (cSt)

$1\ m^2/s = 1{,}000{,}000$ cSt

Fluids for which the shearing stress is linearly related to the rate of shearing strain are designated as Newtonian fluids, as shown in Figure 5.

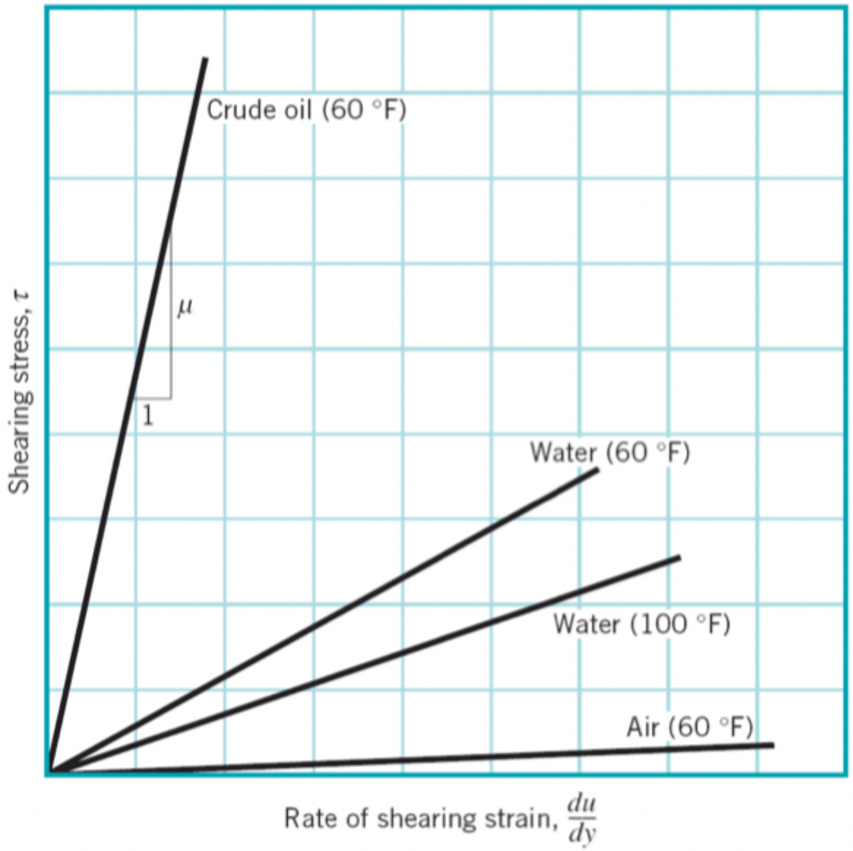


Figure 5: The relation of shearing stress for Newtonian fluid.

Fluids for which the shearing stress is not linearly related to the rate of shearing strain are designated as non-Newtonian fluids, as shown in Figure 6.

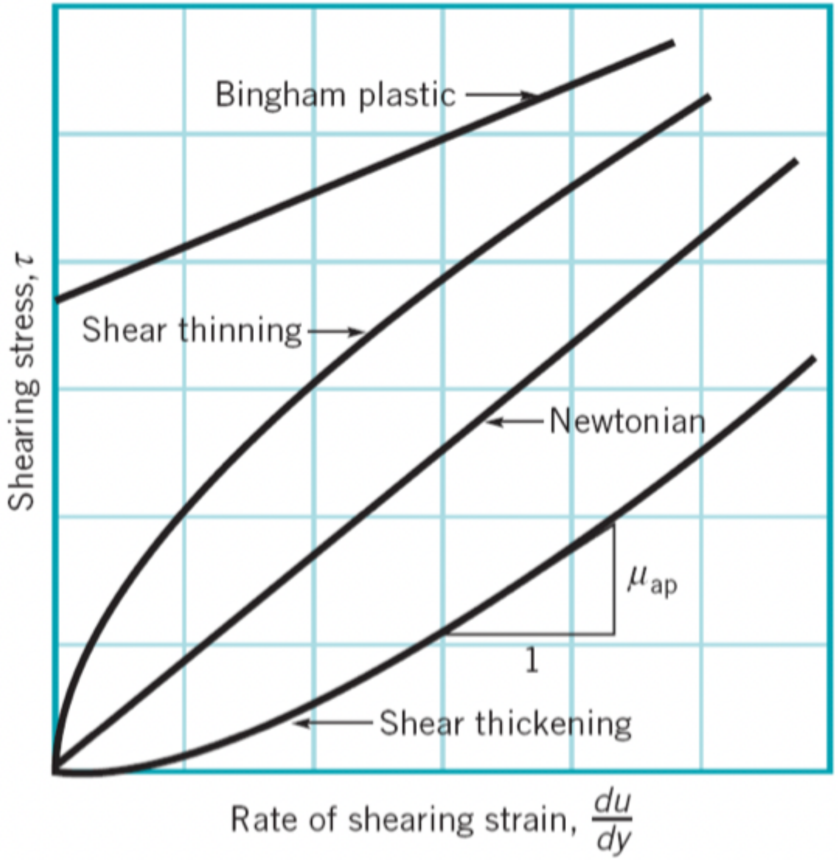


Figure 6: The relation of shearing stress for non-Newtonian fluid.

Shear thinning (Pseudoplastic fluid)

In fluid mechanics, shear thinning is the non-Newtonian behavior of fluids whose viscosity decreases under shear strain.

During the process of shearing in polymer fluids, long molecules that are randomly oriented and with no connected structure tend to align, giving a reduction in apparent viscosity. In emulsions a drop in viscosity is due to orientation and deformation of the emulsion particles. The process is usually reversible.

Modern paints are examples of pseudoplastic materials. When modern paints are applied, the shear created by the brush or roller will allow them to thin and wet out the surface evenly. Once applied, the paints regain their higher viscosity, which avoids drips and runs.

Ketchup is a prominent example of a shear thinning material, being viscous when at rest, but flows at speed when agitated by squeezing, shaking or striking the bottle.

Whipped cream is also an example of a shear thinning material. When whipped cream is sprayed out of its canister, it flows out smoothly from the nozzle due to the low viscosity at high flow rate. However, after whipped cream is sprayed into a spoon, it does not flow, and its increased viscosity allows it to be rigid.

Shear thickening (Dilatancy fluid)

A shear thickening or dilatant fluid is one in which viscosity increases with the rate of shear strain. This type of fluids are usually suspensions with a high solid content.

This can readily be seen with a mixture of corn starch and water which acts in counterintuitive ways when struck or thrown against a surface.

The increase in viscosity with shear rate is attributed to the rearranging of the particles suspended in the fluid, resulting in the dilation of voids between the particles. This behavior can be related to the arrangement of the fluid molecules.

The theory is that in the non-shear condition molecules adopt a close packed formation, which gives the minimum volume of voids. When shear is applied the molecules move to an open pack formation, dilating the voids. As a result, there is an insufficient amount of fluid to fill the voids, giving an increased resistance to flow.

Sand that is completely soaked with water also behaves as a dilatant material. This is the reason why when walking on wet sand, a dry area appears directly underfoot.

Thixotropic behavior

Thixotropic behavior, also known in the literature as shear duration thinning, is shown in Figure 7. It is associated with a loss of consistency of the fluid as the duration of shear increases.

During the process of shearing, it is believed that the structure of the thixotropic fluid is being broken down. The destruction of the fluid structure progresses with time, giving a reduction in apparent viscosity, until a certain balance is reached where the structure rebuilds itself at the same rate as it is destroyed.

At this stage the apparent viscosity attains a steady value. In some cases the process is reversible, i.e., viscosity returns to its original value when shear is removed, but permanent viscosity loss is also possible.

A converse effect to thixotropic behavior, i.e., thickening of the fluid with the duration of shearing, can also occur with some fluids. This phenomenon is known in the literature as inverse thixotropy or rheopectic behavior.

An example of a fluid with such properties is synovial fluid, a natural lubricant found in human and animal joints. It was found that the viscosity of synovial fluid increases with the duration of shearing. It seems that the longer the duration of shearing the better the lubricating film which is generated by the body.

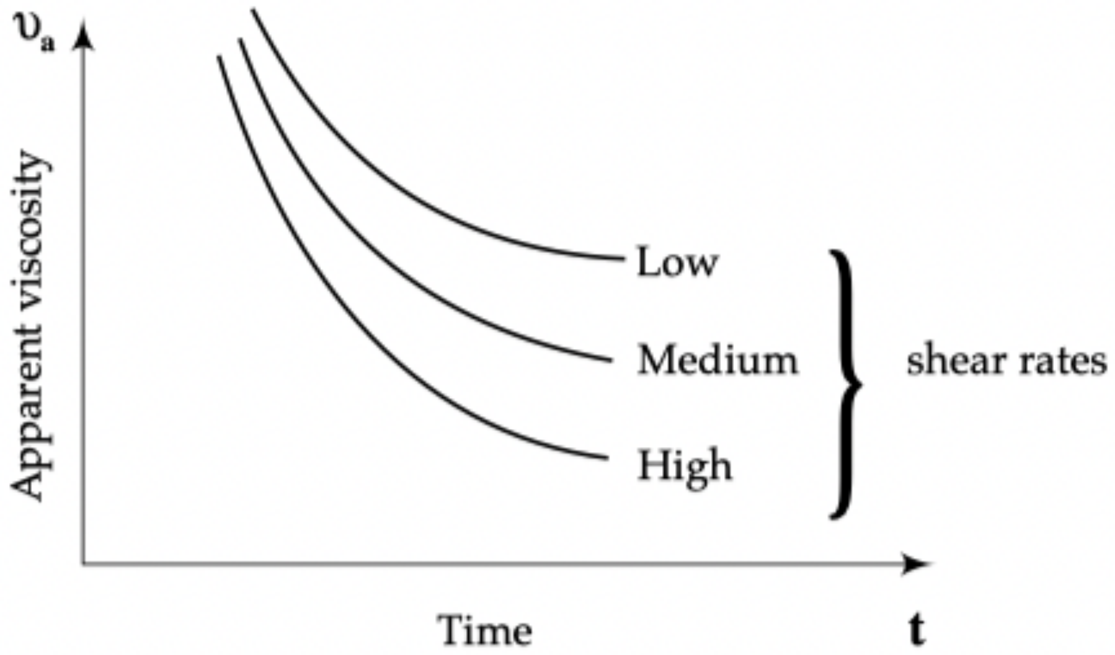


Figure 7: Thixotropic behavior.

Viscosity temperature relationship

The viscosity of lubricating oils is extremely sensitive to the operating temperature. With increasing temperature the viscosity of oils falls quite rapidly. In some cases the viscosity of oil can fall by about 80% with a temperature increase of 25°C.

From the engineering viewpoint it is important to know the viscosity at the operating temperature since it influences the lubricant film thickness separating two surfaces.

The oil viscosity at a specific temperature can be either calculated from the viscosity-temperature equation or obtained from the viscosity-temperature ASTM chart.

Viscosity-temperature equations

There are several viscosity-temperature equations available. Some of them are purely empirical while others are derived from theoretical models.

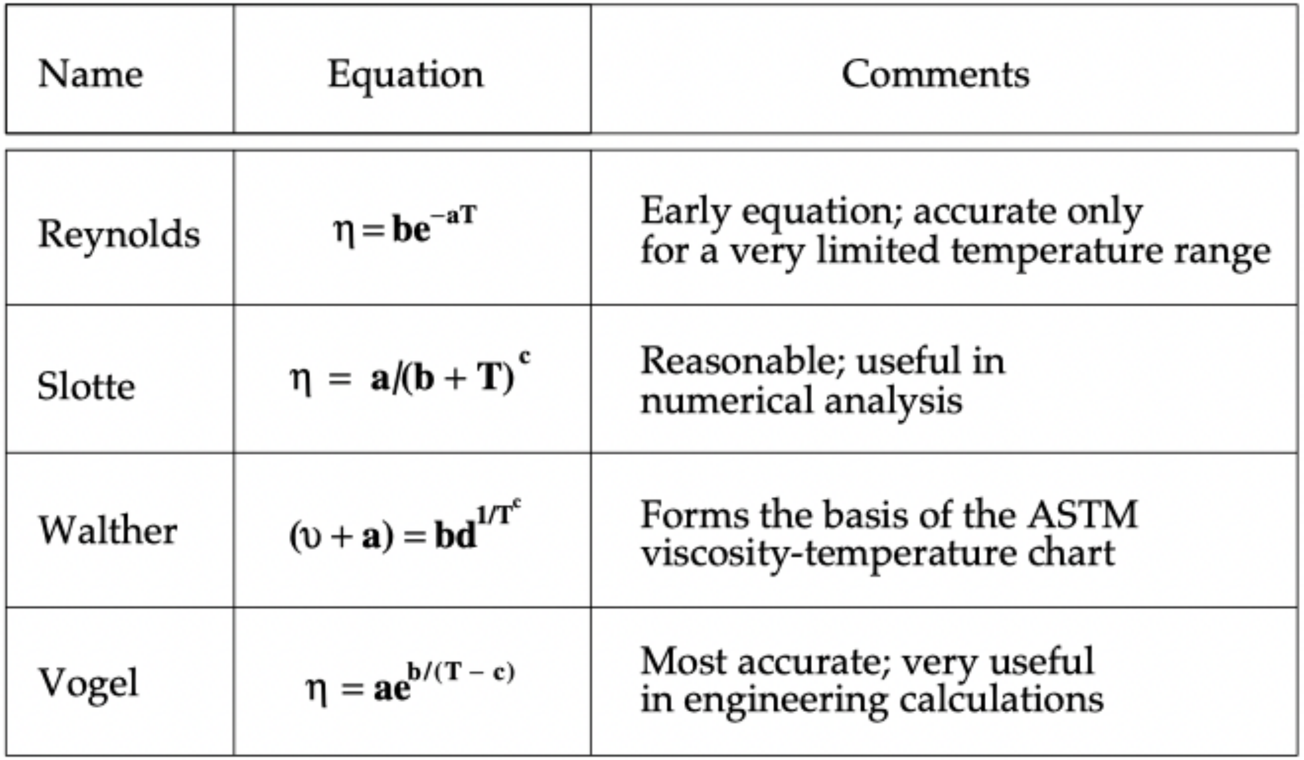
The most commonly used equations are summarized in Table 2.

The most accurate of these is the Vogel equation.

Three viscosity measurements at different temperatures for a specific oil are needed in order to determine the three constants in this equation. The oil viscosity can then be calculated at the required temperature, or the operating temperature can be calculated if the viscosity is known.

Apart from being very accurate the Vogel equation is useful in numerical analysis. A computer program “VISCOSITY” for the Vogel equation is commonly used in industry. Based on the three temperature-viscosity measurements the program calculates the viscosity at the required temperature. It also includes the option for the calculation of temperature corresponding to a given viscosity.

Table 2: Viscosity-temperature equations



Name	Equation	Comments
Reynolds	$\eta = \mathbf{b}\mathbf{e}^{-\mathbf{a}\mathbf{T}}$	Early equation; accurate only for a very limited temperature range
Slotte	$\eta = \mathbf{a}/(\mathbf{b} + \mathbf{T})^{\mathbf{c}}$	Reasonable; useful in numerical analysis
Walther	$(\upsilon + \mathbf{a}) = \mathbf{b}\mathbf{d}^{1/\mathbf{T}^{\mathbf{c}}}$	Forms the basis of the ASTM viscosity-temperature chart
Vogel	$\eta = \mathbf{a}\mathbf{e}^{\mathbf{b}/(\mathbf{T} - \mathbf{c})}$	Most accurate; very useful in engineering calculations

Viscosity-temperature chart

The most widely used chart is the ASTM (American Society for Testing Materials) Viscosity-temperature chart (ASTM D341), which is entirely empirical and is based on Walther's equation found in Table 2.

$$(\upsilon + a) = bd^{1/T^c}$$

In deriving the bases for the ASTM chart, logs were taken from Walther's equation and " d " was assumed to equal 10. The equation was then written in the form:

log 10(υ + a) = log 10b + 1/Tc

$$\log_{10}(\upsilon + a) = \log_{10} b + \frac{1}{T^c}$$

Despite this the ASTM chart is quite successful and works very well for mineral and synthetic oils under normal conditions. It is so well standardized that the viscosity-temperature characteristics are sometimes specified as "ASTM slope".

Viscosity index

Different oils may have different ASTM slopes as shown in Figure 2. As early as 1920 it was known that Pennsylvania crude oils were better than the Gulf Coast (Texan) crude oils. Pennsylvania crude had the best viscosity temperature characteristics while the Gulf Coast crude had the worst since its viscosity varied much more with temperature.

From the engineering viewpoint there was a need for a parameter which would accurately describe the viscosity-temperature characteristics of the oils.

In 1929 a “Viscosity Index” was developed by Dean and Davis.

The viscosity index is an entirely empirical parameter that compares the kinematic viscosity of the oil of interest to the viscosities of two reference oils that have a considerable difference in sensitivity of viscosity to temperature.

The reference oils have been selected in such a way that one has a viscosity index equal to zero (VI=0) and the other has a viscosity index equal to one hundred (VI=100) at 100°F (37.8°C), but they both have the same viscosity as the oil of interest at 210°F (98.89°C), as illustrated in Figure 7.

Since Pennsylvania and Gulf Coast oils have the same viscosity at 210°F (98.9°C) they were initially selected as reference oils. Oils made from Pennsylvania crude were assigned the viscosity index of 100 whereas oils made from the Gulf Coast crude the viscosity index of 0.

The viscosity index can be calculated from the following formula:

$$VI = \frac{L - U}{L - H} \times 100$$

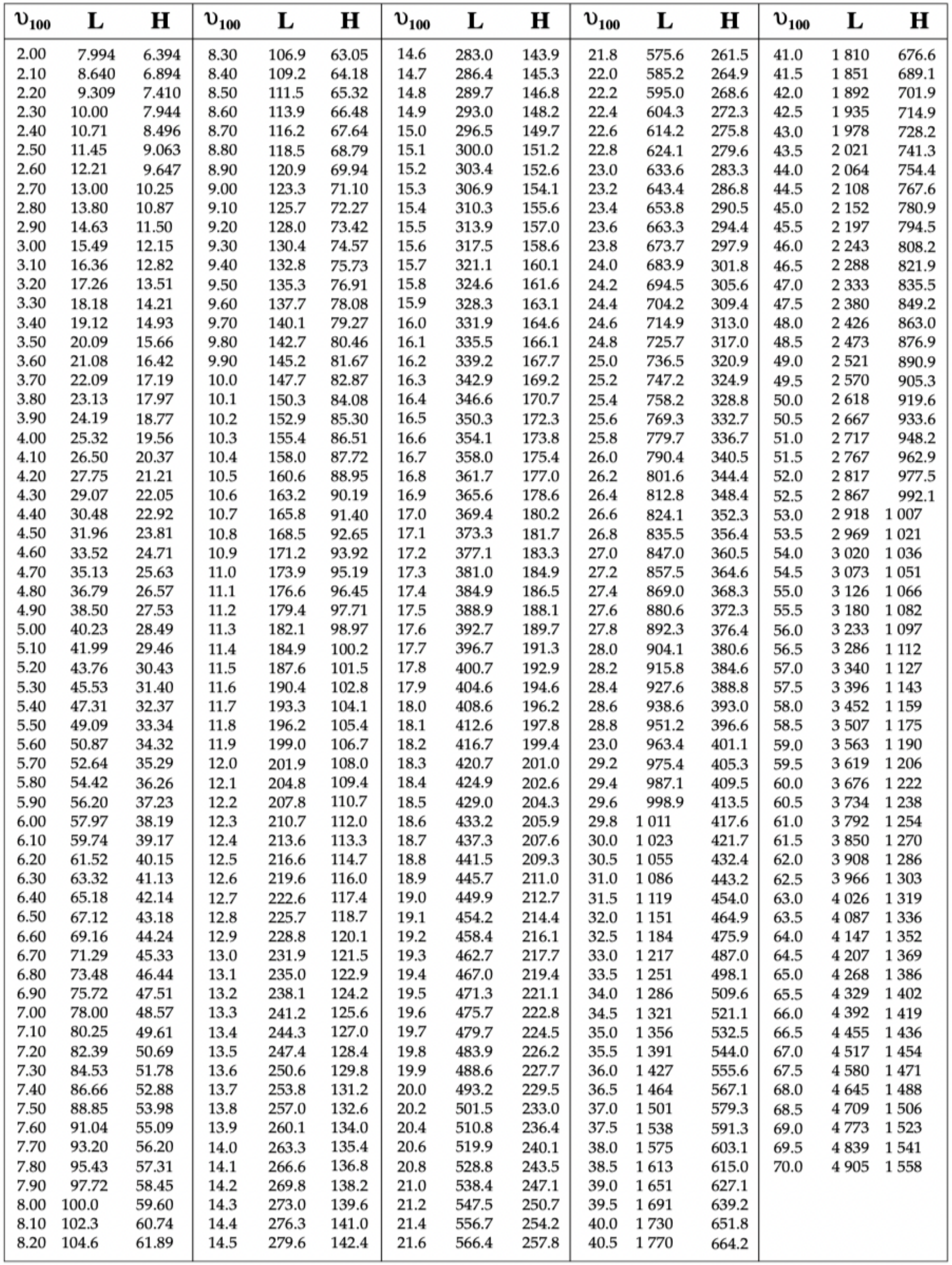
Firstly the kinematic viscosity of the oil of interest is measured at 40°C (U) and at 100°C.

Then the values of “L” and “H” that correspond to the viscosity at 100°C of the oil of interest are read from Table 3 (ASTM D2270).

Substituting the obtained values of “U”, “L” and “H” into the above equation yields the viscosity index.

Table 3:
Data for the evaluation
of viscosity index.

υ_{100} is the kinematic viscosity of the oil of interest at 100°C in centiStokes.



υ_{100}	L	H	υ_{100}	L	H	υ_{100}	L	H	υ_{100}	L	H	υ_{100}	L	H
2.00	7.994	6.394	8.30	106.9	63.05	14.6	283.0	143.9	21.8	575.6	261.5	41.0	1 810	676.6
2.10	8.640	6.894	8.40	109.2	64.18	14.7	286.4	145.3	22.0	585.2	264.9	41.5	1 851	689.1
2.20	9.309	7.410	8.50	111.5	65.32	14.8	289.7	146.8	22.2	595.0	268.6	42.0	1 892	701.9
2.30	10.00	7.944	8.60	113.9	66.48	14.9	293.0	148.2	22.4	604.3	272.3	42.5	1 935	714.9
2.40	10.71	8.496	8.70	116.2	67.64	15.0	296.5	149.7	22.6	614.2	275.8	43.0	1 978	728.2
2.50	11.45	9.063	8.80	118.5	68.79	15.1	300.0	151.2	22.8	624.1	279.6	43.5	2 021	741.3
2.60	12.21	9.647	8.90	120.9	69.94	15.2	303.4	152.6	23.0	633.6	283.3	44.0	2 064	754.4
2.70	13.00	10.25	9.00	123.3	71.10	15.3	306.9	154.1	23.2	643.4	286.8	44.5	2 108	767.6
2.80	13.80	10.87	9.10	125.7	72.27	15.4	310.3	155.6	23.4	653.8	290.5	45.0	2 152	780.9
2.90	14.63	11.50	9.20	128.0	73.42	15.5	313.9	157.0	23.6	663.3	294.4	45.5	2 197	794.5
3.00	15.49	12.15	9.30	130.4	74.57	15.6	317.5	158.6	23.8	673.7	297.9	46.0	2 243	808.2
3.10	16.36	12.82	9.40	132.8	75.73	15.7	321.1	160.1	24.0	683.9	301.8	46.5	2 288	821.9
3.20	17.26	13.51	9.50	135.3	76.91	15.8	324.6	161.6	24.2	694.5	305.6	47.0	2 333	835.5
3.30	18.18	14.21	9.60	137.7	78.08	15.9	328.3	163.1	24.4	704.2	309.4	47.5	2 380	849.2
3.40	19.12	14.93	9.70	140.1	79.27	16.0	331.9	164.6	24.6	714.9	313.0	48.0	2 426	863.0
3.50	20.09	15.66	9.80	142.7	80.46	16.1	335.5	166.1	24.8	725.7	317.0	48.5	2 473	876.9
3.60	21.08	16.42	9.90	145.2	81.67	16.2	339.2	167.7	25.0	736.5	320.9	49.0	2 521	890.9
3.70	22.09	17.19	10.0	147.7	82.87	16.3	342.9	169.2	25.2	747.2	324.9	49.5	2 570	905.3
3.80	23.13	17.97	10.1	150.3	84.08	16.4	346.6	170.7	25.4	758.2	328.8	50.0	2 618	919.6
3.90	24.19	18.77	10.2	152.9	85.30	16.5	350.3	172.3	25.6	769.3	332.7	50.5	2 667	933.6
4.00	25.32	19.56	10.3	155.4	86.51	16.6	354.1	173.8	25.8	779.7	336.7	51.0	2 717	948.2
4.10	26.50	20.37	10.4	158.0	87.72	16.7	358.0	175.4	26.0	790.4	340.5	51.5	2 767	962.9
4.20	27.75	21.21	10.5	160.6	88.95	16.8	361.7	177.0	26.2	801.6	344.4	52.0	2 817	977.5
4.30	29.07	22.05	10.6	163.2	90.19	16.9	365.6	178.6	26.4	812.8	348.4	52.5	2 867	992.1
4.40	30.48	22.92	10.7	165.8	91.40	17.0	369.4	180.2	26.6	824.1	352.3	53.0	2 918	1 007
4.50	31.96	23.81	10.8	168.5	92.65	17.1	373.3	181.7	26.8	835.5	356.4	53.5	2 969	1 021
4.60	33.52	24.71	10.9	171.2	93.92	17.2	377.1	183.3	27.0	847.0	360.5	54.0	3 020	1 036
4.70	35.13	25.63	11.0	173.9	95.19	17.3	381.0	184.9	27.2	857.5	364.6	54.5	3 073	1 051
4.80	36.79	26.57	11.1	176.6	96.45	17.4	384.9	186.5	27.4	869.0	368.3	55.0	3 126	1 066
4.90	38.50	27.53	11.2	179.4	97.71	17.5	388.9	188.1	27.6	880.6	372.3	55.5	3 180	1 082
5.00	40.23	28.49	11.3	182.1	98.97	17.6	392.7	189.7	27.8	892.3	376.4	56.0	3 233	1 097
5.10	41.99	29.46	11.4	184.9	100.2	17.7	396.7	191.3	28.0	904.1	380.6	56.5	3 286	1 112
5.20	43.76	30.43	11.5	187.6	101.5	17.8	400.7	192.9	28.2	915.8	384.6	57.0	3 340	1 127
5.30	45.53	31.40	11.6	190.4	102.8	17.9	404.6	194.6	28.4	927.6	388.8	57.5	3 396	1 143
5.40	47.31	32.37	11.7	193.3	104.1	18.0	408.6	196.2	28.6	938.6	393.0	58.0	3 452	1 159
5.50	49.09	33.34	11.8	196.2	105.4	18.1	412.6	197.8	28.8	951.2	396.6	58.5	3 507	1 175
5.60	50.87	34.32	11.9	199.0	106.7	18.2	416.7	199.4	23.0	963.4	401.1	59.0	3 563	1 190
5.70	52.64	35.29	12.0	201.9	108.0	18.3	420.7	201.0	29.2	975.4	405.3	59.5	3 619	1 206
5.80	54.42	36.26	12.1	204.8	109.4	18.4	424.9	202.6	29.4	987.1	409.5	60.0	3 676	1 222
5.90	56.20	37.23	12.2	207.8	110.7	18.5	429.0	204.3	29.6	998.9	413.5	60.5	3 734	1 238
6.00	57.97	38.19	12.3	210.7	112.0	18.6	433.2	205.9	29.8	1 011	417.6	61.0	3 792	1 254
6.10	59.74	39.17	12.4	213.6	113.3	18.7	437.3	207.6	30.0	1 023	421.7	61.5	3 850	1 270
6.20	61.52	40.15	12.5	216.6	114.7	18.8	441.5	209.3	30.5	1 055	432.4	62.0	3 908	1 286
6.30	63.32	41.13	12.6	219.6	116.0	18.9	445.7	211.0	31.0	1 086	443.2	62.5	3 966	1 303
6.40	65.18	42.14	12.7	222.6	117.4	19.0	449.9	212.7	31.5	1 119	454.0	63.0	4 026	1 319
6.50	67.12	43.18	12.8	225.7	118.7	19.1	454.2	214.4	32.0	1 151	464.9	63.5	4 087	1 336
6.60	69.16	44.24	12.9	228.8	120.1	19.2	458.4	216.1	32.5	1 184	475.9	64.0	4 147	1 352
6.70	71.29	45.33	13.0	231.9	121.5	19.3	462.7	217.7	33.0	1 217	487.0	64.5	4 207	1 369
6.80	73.48	46.44	13.1	235.0	122.9	19.4	467.0	219.4	33.5	1 251	498.1	65.0	4 268	1 386
6.90	75.72	47.51	13.2	238.1	124.2	19.5	471.3	221.1	34.0	1 286	509.6	65.5	4 329	1 402
7.00	78.00	48.57	13.3	241.2	125.6	19.6	475.7	222.8	34.5	1 321	521.1	66.0	4 392	1 419
7.10	80.25	49.61	13.4	244.3	127.0	19.7	479.7	224.5	35.0	1 356	532.5	66.5	4 455	1 436
7.20	82.39	50.69	13.5	247.4	128.4	19.8	483.9	226.2	35.5	1 391	544.0	67.0	4 517	1 454
7.30	84.53	51.78	13.6	250.6	129.8	19.9	488.6	227.7	36.0	1 427	555.6	67.5	4 580	1 471
7.40	86.66	52.88	13.7	253.8	131.2	20.0	493.2	229.5	36.5	1 464	567.1	68.0	4 645	1 488
7.50	88.85	53.98	13.8	257.0	132.6	20.2	501.5	233.0	37.0	1 501	579.3	68.5	4 709	1 506
7.60	91.04	55.09	13.9	260.1	134.0	20.4	510.8	236.4	37.5	1 538	591.3	69.0	4 773	1 523
7.70	93.20	56.20	14.0	263.3	135.4	20.6	519.9	240.1	38.0	1 575	603.1	69.5	4 839	1 541
7.80	95.43	57.31	14.1	266.6	136.8	20.8	528.8	243.5	38.5	1 613	615.0	70.0	4 905	1 558
7.90	97.72	58.45	14.2	269.8	138.2	21.0	538.4	247.1	39.0	1 651	627.1			
8.00	100.0	59.60	14.3	273.0	139.6	21.2	547.5	250.7	39.5	1 691	639.2			
8.10	102.3	60.74	14.4	276.3	141.0	21.4	556.7	254.2	40.0	1 730	651.8			
8.20	104.6	61.89	14.5	279.6	142.4	21.6	566.4	257.8	40.5	1 770	664.2			

One of the problems associated with available formulae is that they are most accurate when calculating the pressure-viscosity coefficients at low shear rates.

In many engineering applications, especially in heavily loaded concentrated contacts, the lubricant operates under very high shear rates and precise values of the pressure-viscosity coefficient are needed for the evaluation of the minimum film thickness.

Fortunately, an accurate value of this coefficient can be determined experimentally

Viscosity measurements

Various viscosity measurement techniques and instruments have been developed over the years. The most commonly used in engineering applications are capillary and rotational viscometers.

In general, capillary viscometers are suitable for fluids with negligible non-Newtonian effects while rotational viscometers are suitable for fluids with significant non-Newtonian effects. Some viscometers have a special heating bath built in, in order to control and measure the temperature, so that the viscosity-temperature characteristics can be obtained.

In most cases water is used in the heating bath. Water is suitable for the temperature range between 0° and 99°C.

For higher temperatures mineral oils are used and for low temperatures down to -54°C, ethyl alcohol or acetone is used.

Capillary viscometers

Capillary viscometers are based on the principle that a specific volume of fluid will flow through the capillary (ASTM D445, ASTM D2161), as shown in Figure 8. The time necessary for this volume of fluid to flow gives the “kinematic viscosity”.

Flow through the capillary must be laminar and the deductions are based on Poiseuille’s law for steady viscous flow in a pipe.

Assuming that the fluids are Newtonian, and neglecting end effects, the kinematic viscosity can be calculated from the formula:

$$\upsilon = \frac{\pi R^4 g H T}{8LV} = k(t_2 - t_1)$$

υ : Kinematic viscosity in mm^2/s
R : Capillary radius in meter
g : Gravity acceleration in m/s^2
H : Mean hydrostatic head in meter
T : Flow time through the capillary in second
L : Capillary length in meter
V : Flow volume in m^3
t_i : Time at i-th location in second

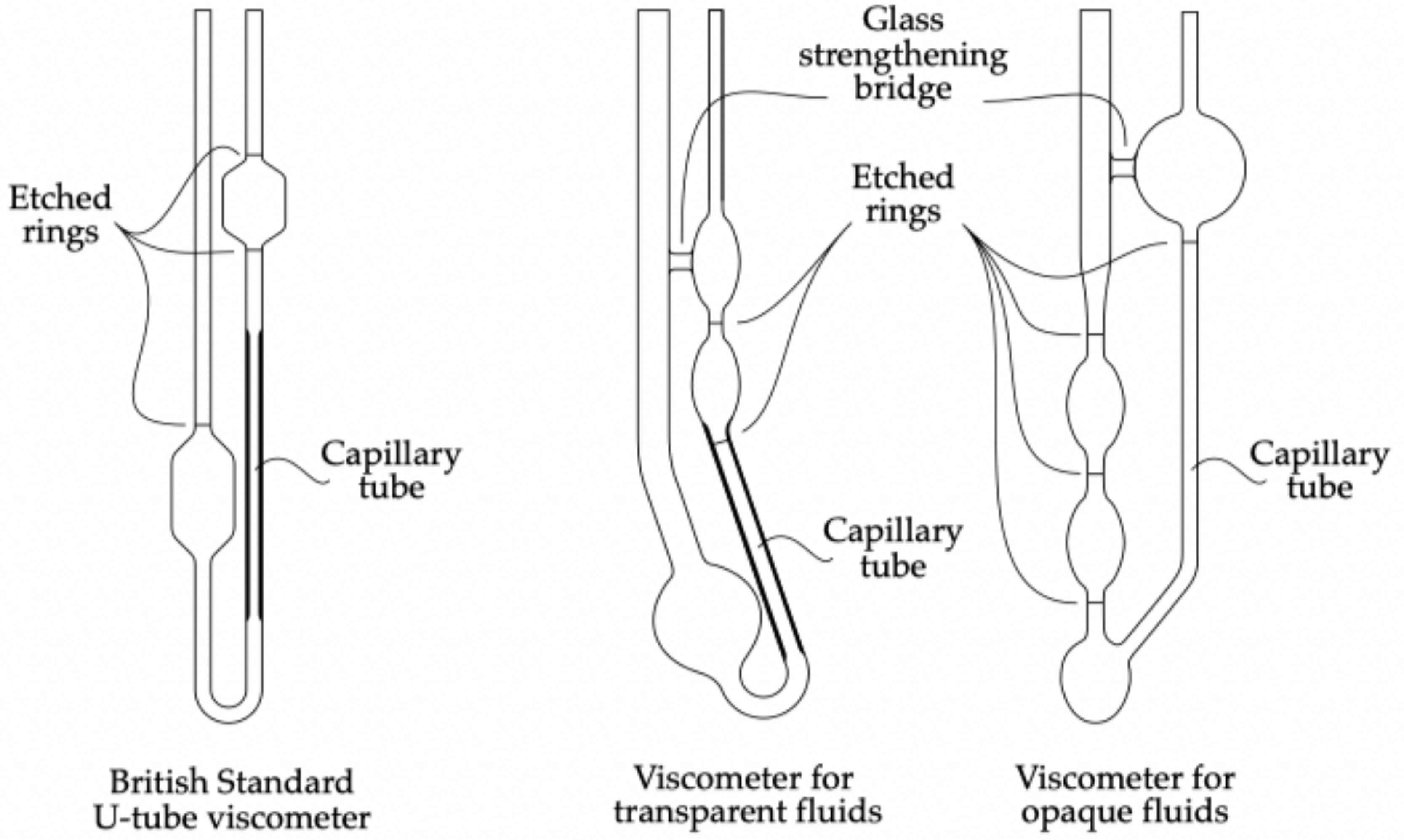


Figure 8: Typical capillary viscometers

In order to measure the viscosity of the fluid by one of the viscometers shown in Figure 8, the container is filled with oil between the etched lines. The measurement is then made by timing the period required for the oil meniscus to flow from the first to the second timing mark. This is measured with an accuracy to within 0.1 second.

Kinematic viscosity can also be measured by so-called “short tube” viscometers. In the literature they are also known as “efflux viscometers”. As in capillary viscometers, viscosity is determined by measuring the time necessary for a given volume of fluid to discharge under gravity through a short tube orifice in the base of the instrument.

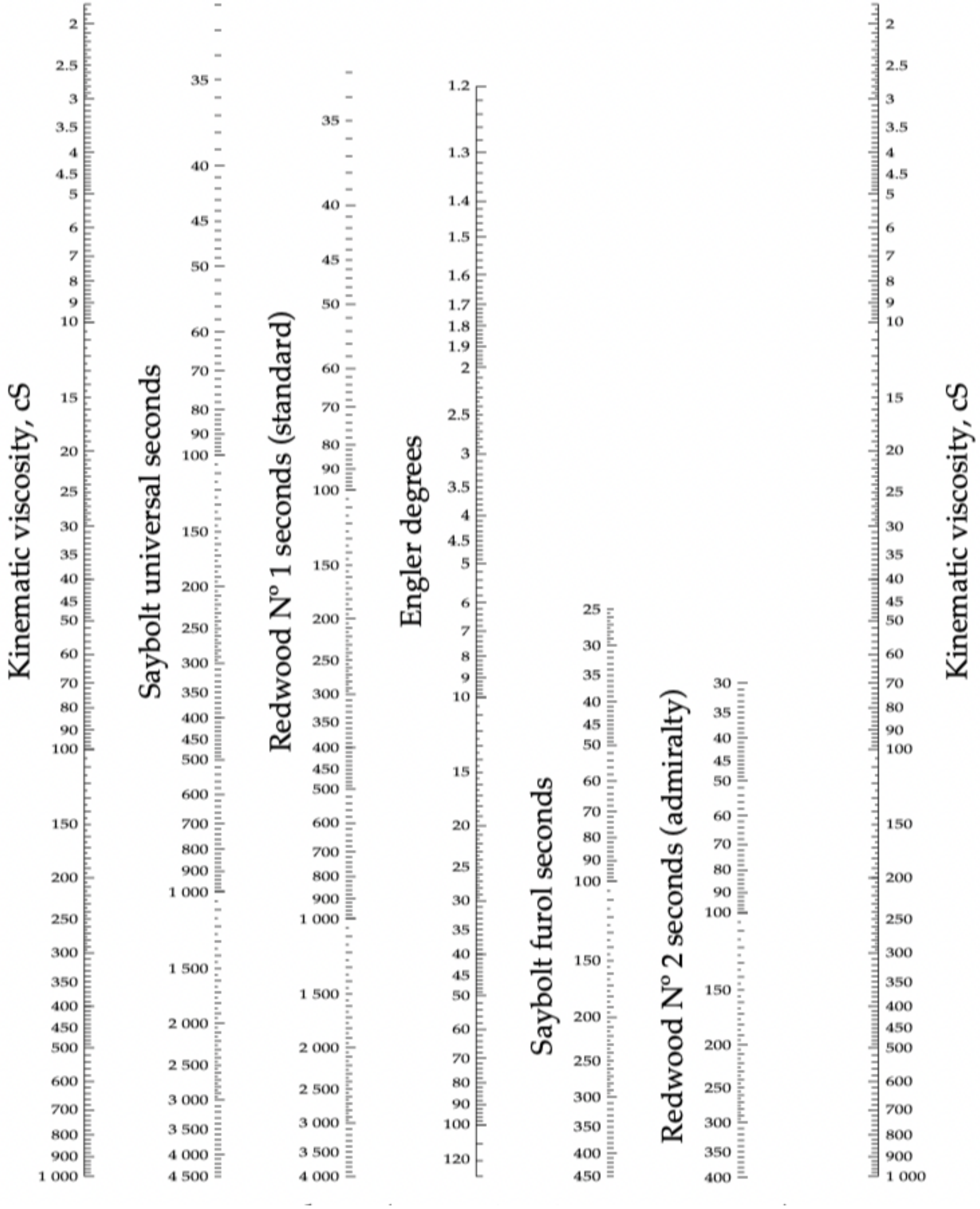
The most commonly used viscometers are Redwood, Saybolt and Engler. The operation principle of these viscometers is the same, and they only differ by the orifice dimensions and the volume of fluid discharged.

Redwood viscometers are used in the United Kingdom, Saybolt in Europe and Engler mainly in former Eastern Europe. The viscosities measured by these viscometers are quoted in terms of the time necessary for the discharge of a certain volume of fluid. Hence the viscosity is sometimes found as being quoted in Redwood and Saybolt seconds.

The viscosity measured on Engler viscometers is quoted in Engler degrees, which is the time for the fluid to discharge divided by the discharge time of the same volume of water at the same temperature. Redwood and Saybolt seconds and Engler degrees can be converted into centistokes as shown in Figure 2.11. These particular types of viscometers are gradually becoming obsolete. A typical short tube viscometer is shown in Figure 9.

In order to extend the range of kinematic, Saybolt Universal, Redwood No. 1 and Engler viscosity scales only (Figure 9), a simple operation is performed. The viscosities on these scales that correspond to the viscosity between 100 and 1,000 (cS) on the kinematic scale are multiplied by a factor of 10, which gives the required extension.

Figure 9:
Viscosity conversion chart.



Rotational viscometers

Rotational viscometers are based on the principle that the fluid viscosity is related to the force required to generate shear between two surfaces separated by a film of fluid (ASTM D2983).

In these viscometers one of the surfaces is stationary and the other is rotated by an external drive and the fluid fills the space in between. The measurements are conducted by applying either a constant torque and measuring the changes in the speed of rotation or applying a constant speed and measuring the changes in the torque. These viscometers give the “dynamic viscosity”. There are three main types of these viscometers: rotating cylinder and cone-on-plate viscometers.

Rotating cylinder viscometer

The rotating cylinder viscometer, also known as a "Couette viscometer", consists of two concentric cylinders with an annular clearance filled with fluid as shown in Figure 10.

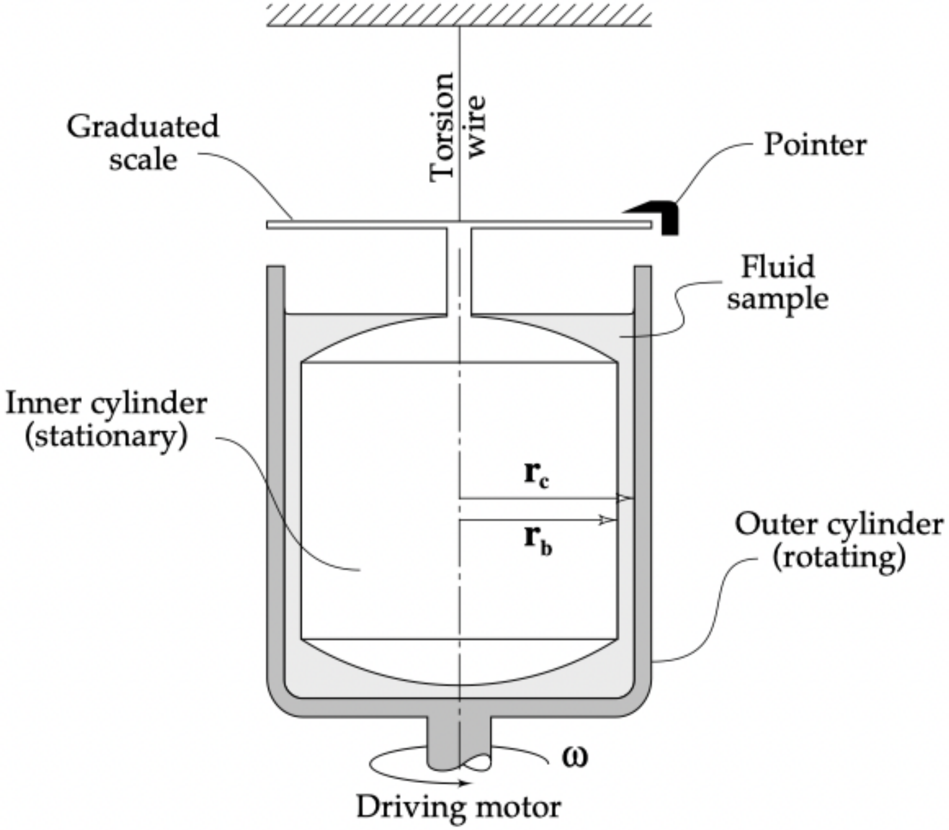


Figure 10: Schematic diagram of a rotating cylinder viscometer.

The inside cylinder is stationary and the outside cylinder rotates at constant velocity. The force necessary to shear the fluid between the cylinders is measured. The velocity of the cylinder can be varied so that the changes in viscosity of the fluid with shear rate can be assessed.

Care needs to be taken with non-Newtonian fluids as these viscometers are calibrated for Newtonian fluids. Different cylinders with a range of radial clearances are used for different fluids. For Newtonian fluids the dynamic viscosity can be estimated from the formula:

$$\mu = \frac{M\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right)}{4\pi D\omega} = k\frac{M}{\omega}$$

μ : Dynamic viscosity in Pa.s.

M : Shear torque on the inner cylinder in N.m.

$R_{1,2}$: Radii of the inner and outer cylinder in meter.

D : Immersion depth of the cylinder in meter.

ω : Angular velocity in rad/s.

k : Viscometer constant, usually supplied by the manufacturer for each pair of cylinder.

Cone on plate viscometer

The cone on plate viscometer consists of a conical surface and a flat plate. Either of these surfaces can be rotated. The clearance between the cone and the plate is filled with the fluid and the cone angle ensures a constant shear rate in the clearance space.

The advantage of this viscometer is that a very small sample volume of fluid is required for the test. In some of these viscometers, the temperature of the fluid sample is controlled during tests. This is achieved by circulating preheated or cooled external fluid through the plate of the viscometer.

These viscometers can be used with both Newtonian and non-Newtonian fluids as the shear rate is approximately constant across the gap. The schematic diagram of this viscometer is shown in Figure 11.

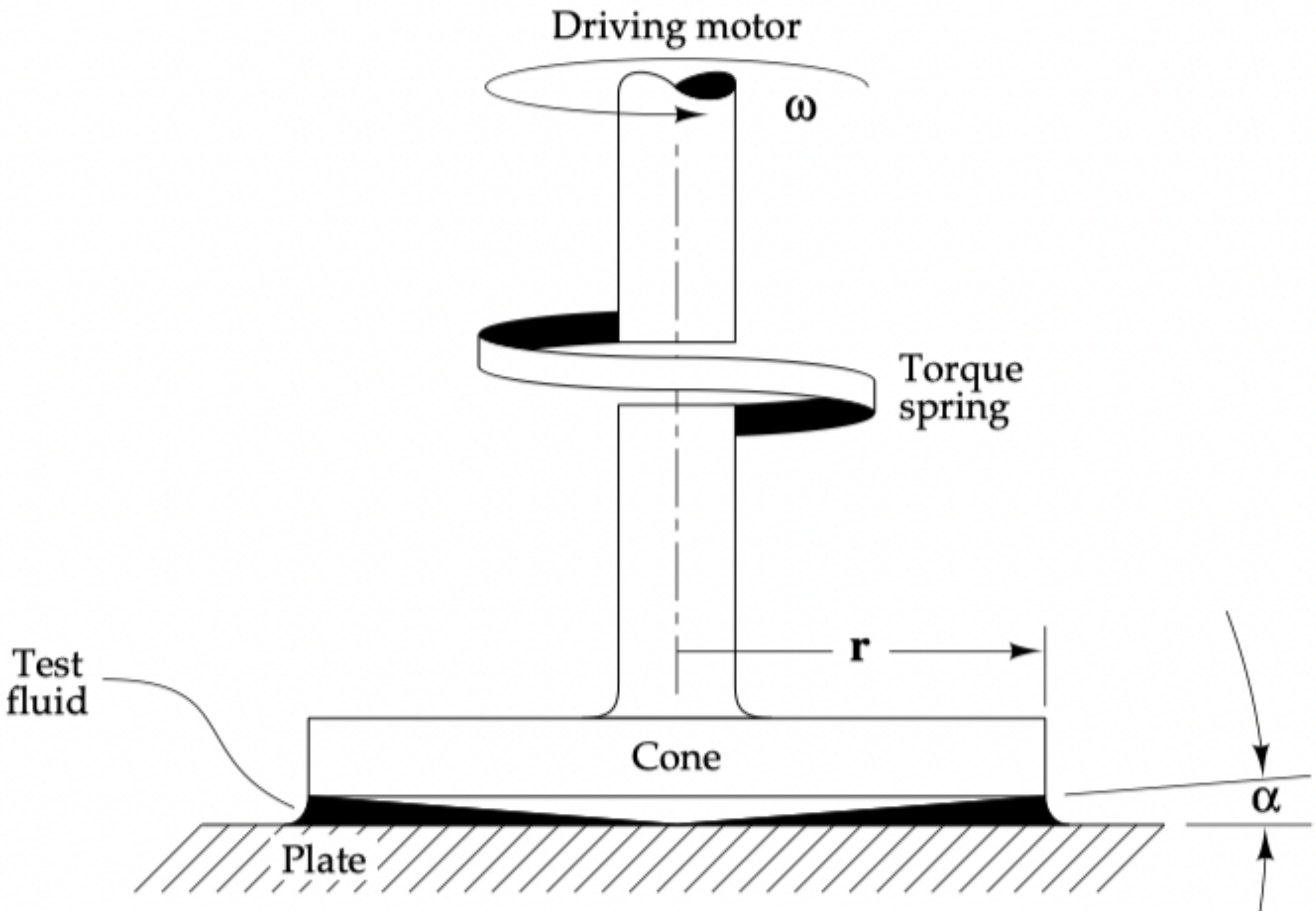


Figure 11: Schematic diagram of a cone on plate viscometer.

Falling ball viscometer

Many other types of viscometers, based on different principles of measurement, are also available. Most commonly used in many laboratories is the “Falling Ball Viscometer”.

A glass tube is filled with the fluid to be tested and a steel ball is dropped into the tube. The measurement is then made by timing the period required for the ball to fall from the first to the second timing mark, etched on the tube. The time is measured with an accuracy to within 0.1 second.

This viscometer can also be used for the determination of viscosity changes under pressure. A schematic diagram of this viscometer is shown in Figure 12.

The dynamic viscosity is estimated from the formula:

$$\mu = \frac{2r^2(\rho_b - \rho)gF}{9V}$$

μ : Dynamic viscosity in Pa.s.
r : Radius of the ball in meter
ρ_b : Density of the ball in kg/m^3
g : Gravity acceleration in m/s^2
ρ : Density of the fluid in kg/m^3
F : Correction factor
V : Velocity of the ball in m/s

The correction factor can be calculated from the formula;

$$F = 1 - 2.104\left(\frac{d}{D}\right) + 2.09\left(\frac{d}{D}\right)^3 - 0.9\left(\frac{d}{D}\right)^5$$

d : Diameter of the ball in meter
D : Internal diameter of the tube in meter

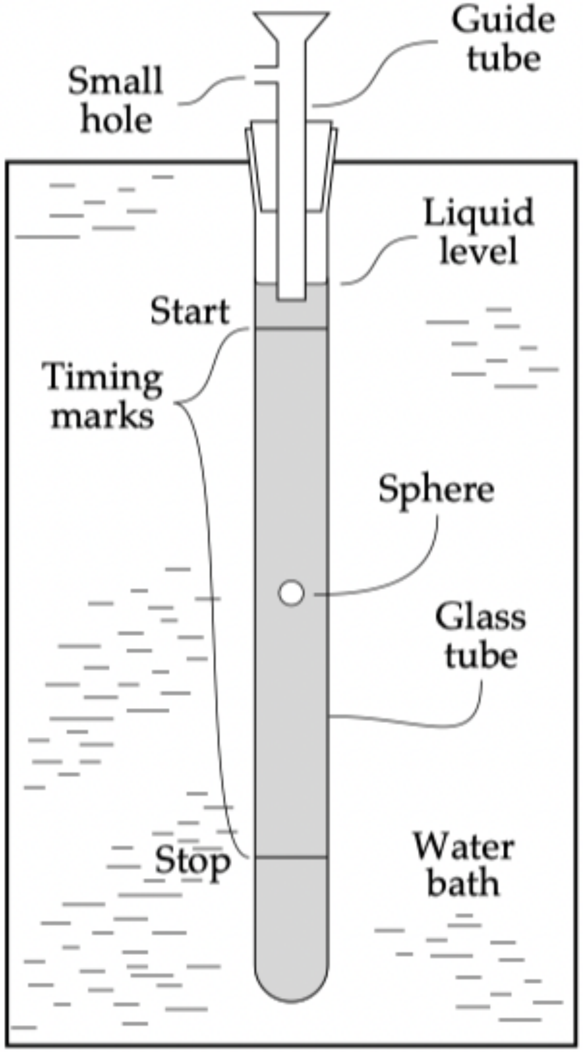


Figure 11: Schematic diagram of a “Falling Ball Viscometer”.

Viscosity of mixtures

In industrial practice it might be necessary to mix two similar fluids of different viscosities in order to achieve a mixture of a certain viscosity. The question is, how much of fluid “A” should be mixed with fluid “B”?

This can simply be worked out by using ASTM viscosity paper with linear abscissa representing percentage quantities of each of the fluids. The viscosity of each of the fluids at the same temperature is marked on the ordinate on each side of the graph as shown in Figure 12.

A straight line is drawn between these points and intersects a horizontal line which corresponds to the required viscosity. A vertical line drawn from the point of intersection crosses the abscissa, indicating the proportions needed of the two fluids.

In the example of Figure 12, 20% of the less viscous component is mixed with 80% of the more viscous component to give the “required viscosity”.

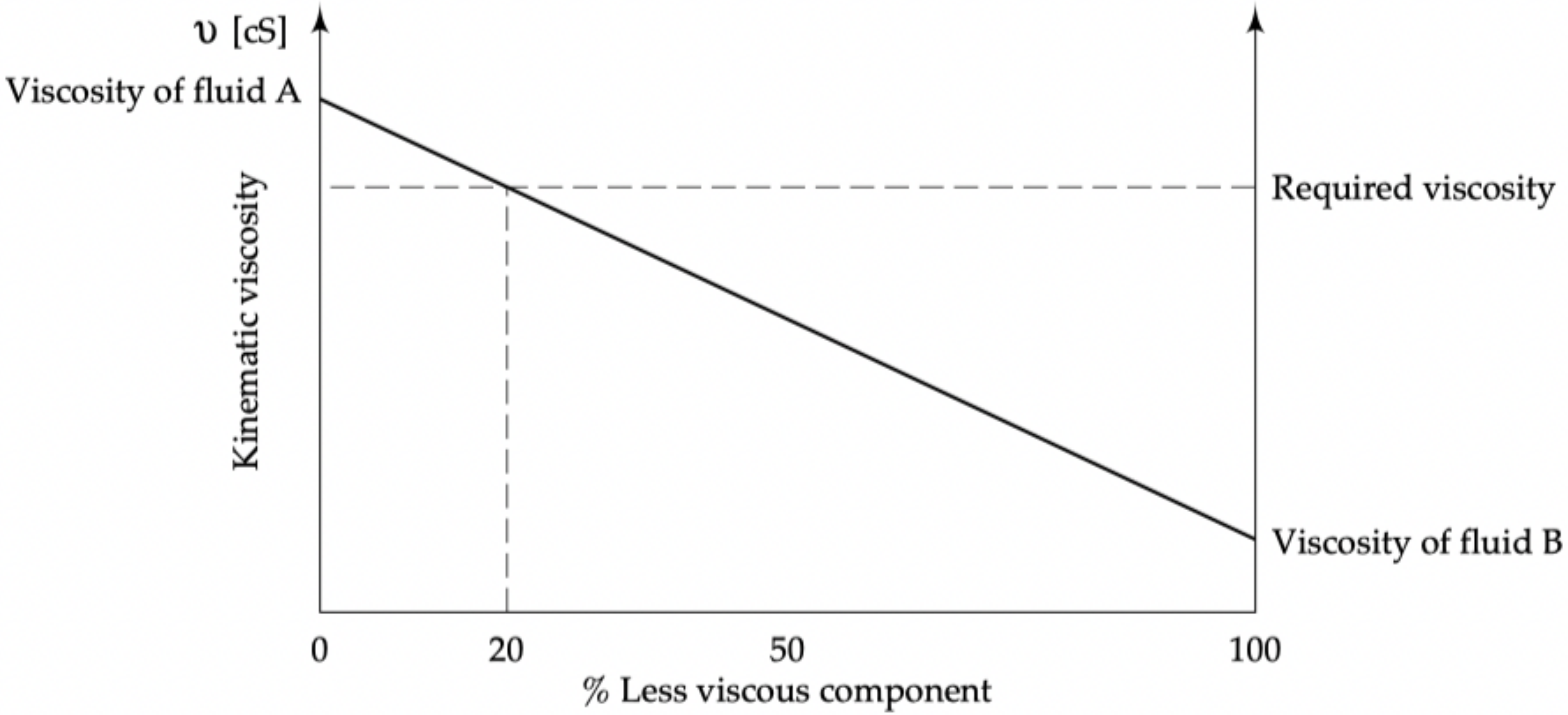


Figure 12: Determining the viscosity of a mixture.

Oil viscosity classification

There are several widely used oil viscosity classifications.

The most commonly used are SAE (Society of Automotive Engineers),

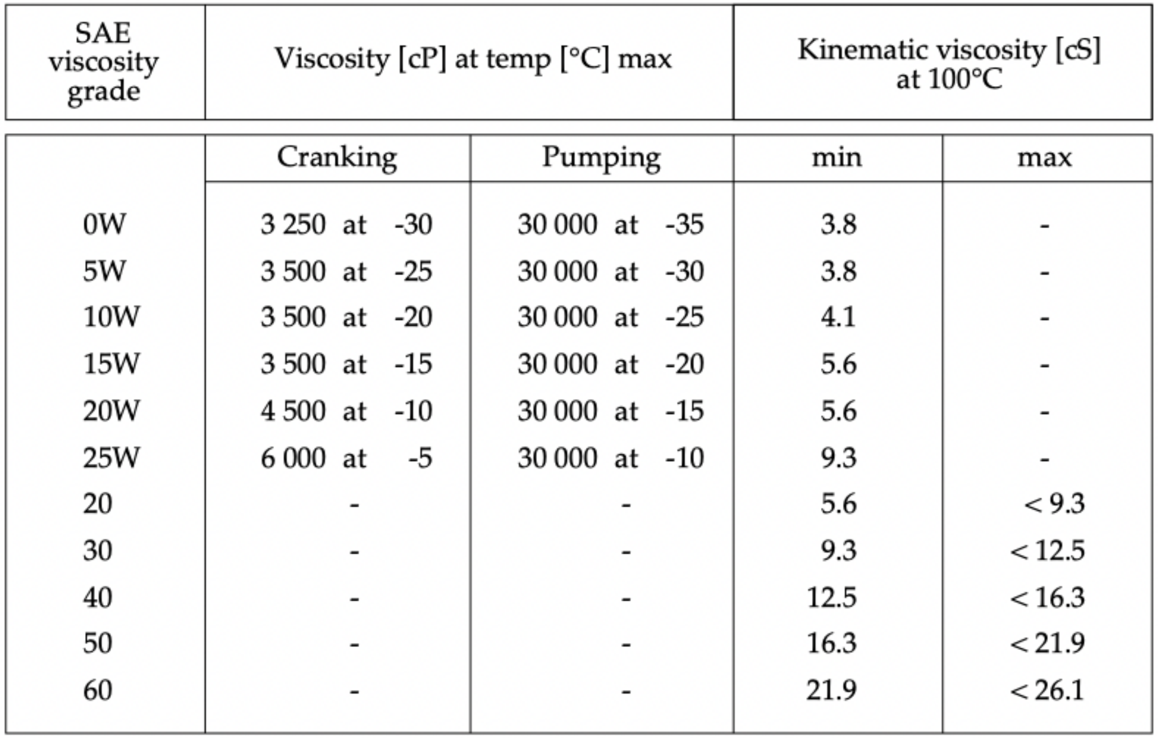
ISO (International Organization for Standardization) and

military specifications.

SAE Viscosity classification

Oils used in combustion engines and power transmissions are graded according to SAE J300 and SAE J306 classifications, respectively. A recent SAE classification establishes eleven (11) engine oil and seven (7) transmission oil grades. Engine oil viscosities for different SAE grades are shown in Table 4.

Table 4: SAE classification of engine oils.



SAE viscosity grade	Viscosity [cP] at temp [°C] max		Kinematic viscosity [cS] at 100°C	
	Cranking	Pumping	min	max
0W	3 250 at -30	30 000 at -35	3.8	-
5W	3 500 at -25	30 000 at -30	3.8	-
10W	3 500 at -20	30 000 at -25	4.1	-
15W	3 500 at -15	30 000 at -20	5.6	-
20W	4 500 at -10	30 000 at -15	5.6	-
25W	6 000 at -5	30 000 at -10	9.3	-
20	-	-	5.6	< 9.3
30	-	-	9.3	< 12.5
40	-	-	12.5	< 16.3
50	-	-	16.3	< 21.9
60	-	-	21.9	< 26.1

Note that the viscosity in column two (Table 4) is the dynamic viscosity while column three shows the kinematic viscosity.

The low temperature viscosity was measured by the “cold-cranking simulator” and is an indicator of cold weather starting ability.

The viscosity measurements at 100°C are related to the normal operating temperature of the engine.

The oils without a “W” suffix are called “monograde oils” since they meet only one SAE grade.

The oils with a “W” suffix, which stands for “winter”, have good cold-starting capabilities. For climates where the temperature regularly drops below zero Celsius, engine and transmission oils are formulated in such a manner that they give low resistance at start, i.e., their viscosity is low at the starting temperature.

Such oils have a higher viscosity index, achieved by adding viscosity improvers (polymeric additives) to the oil and are called “multigrade oils”. For example, SAE 20W/50 has a viscosity of SAE 20 at -18°C and viscosity of SAE 50 at 100°C as is illustrated in Figure 13.

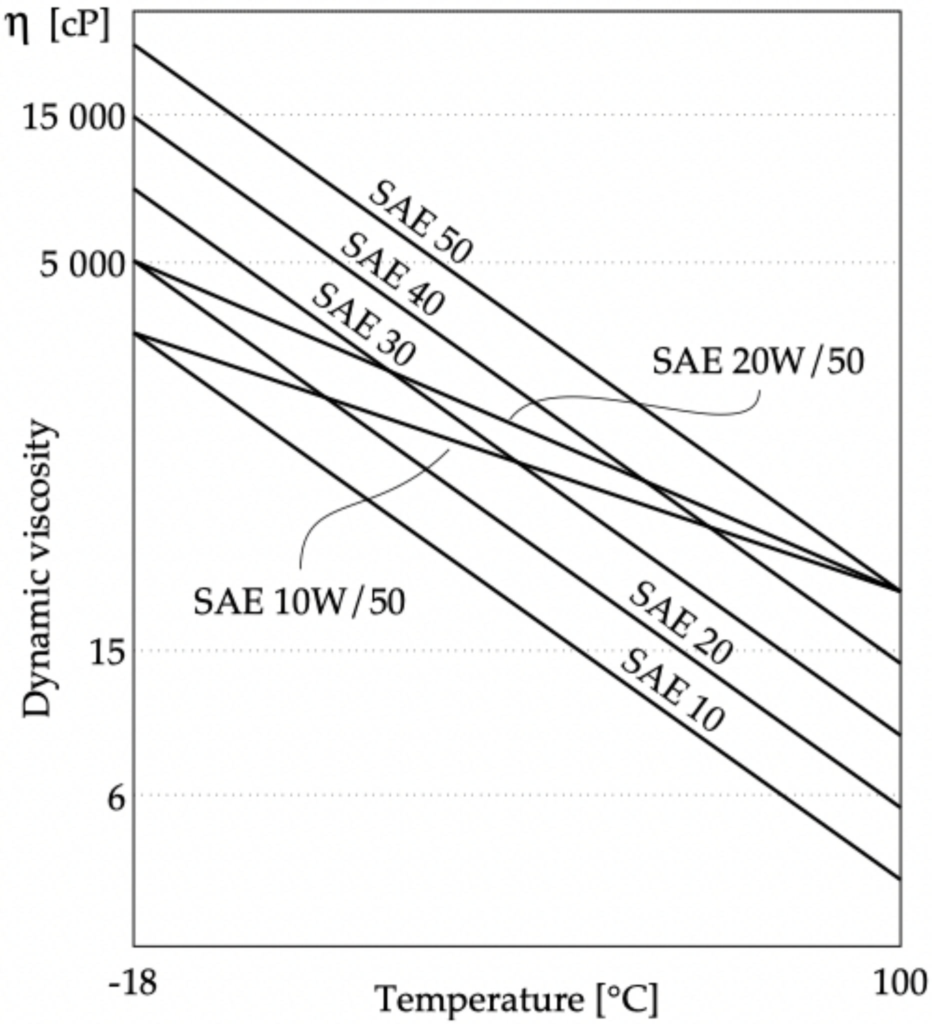


Figure 13: Viscosity-temperature graph for some monograde and multigrade oils (not to scale).

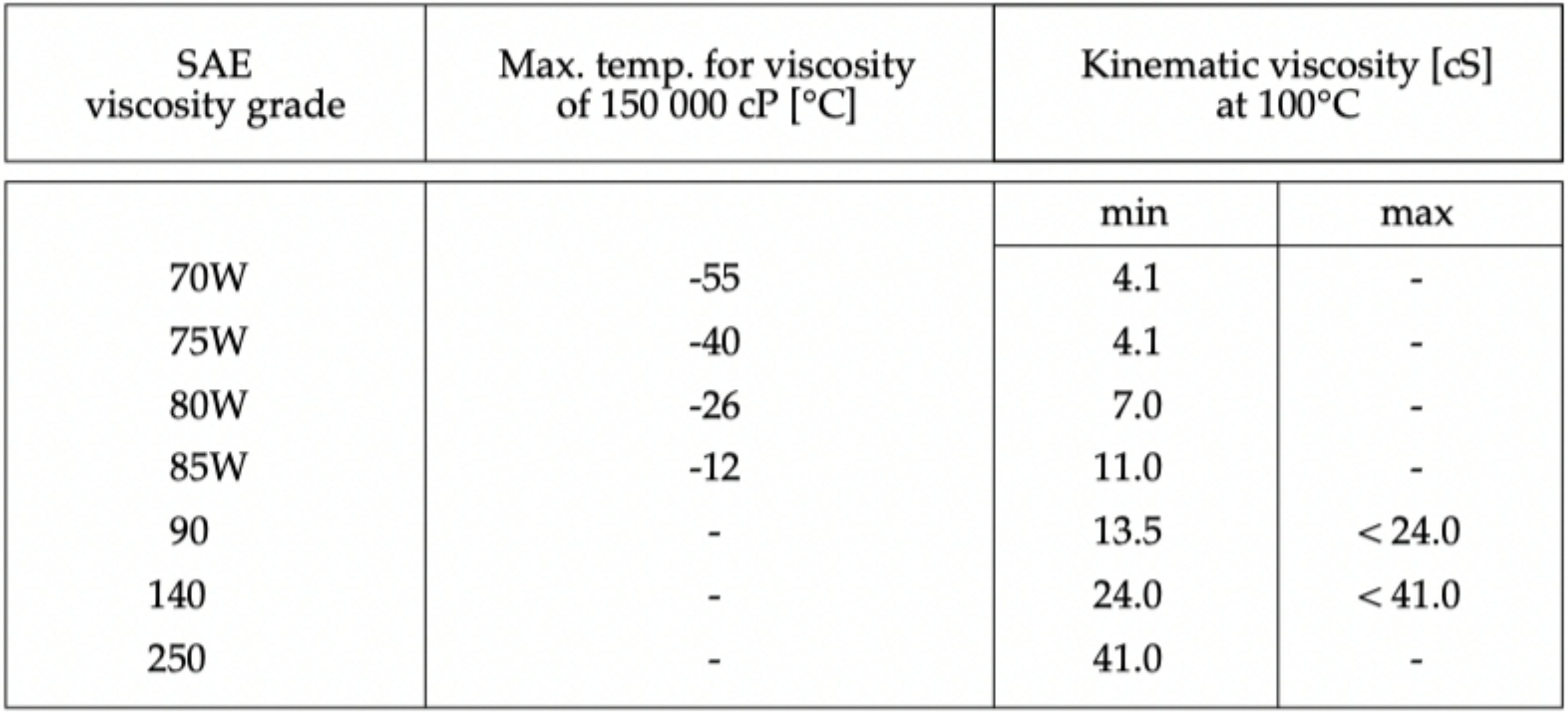
The problem associated with the use of multigrade oils is that they usually shear thin, i.e., their viscosity drops significantly with increased shear rates, due to the polymeric additives.

This has to be taken into account when designing machine components lubricated by these oils. The drop in viscosity can be significant, and with some viscosity improvers even a permanent viscosity loss at high shear rates may occur due to the breaking up of molecules into smaller units. The viscosity loss affects the thickness of the lubricating film and subsequently affects the performance of the machine.

SAE classification of transmission oils is very similar to that of engine oils. The only difference is that the winter grade is defined by the temperature at which the oil reaches the viscosity of 150,000 [cP].

This is the maximum oil viscosity that can be used without causing damage to gears. The classification also permits multigrading. The transmission oil viscosities for different SAE grades are shown in Table 5.

Table 5: SAE classification of transmission oils.



SAE viscosity grade	Max. temp. for viscosity of 150 000 cP [°C]	Kinematic viscosity [cS] at 100°C	
		min	max
70W	-55	4.1	-
75W	-40	4.1	-
80W	-26	7.0	-
85W	-12	11.0	-
90	-	13.5	< 24.0
140	-	24.0	< 41.0
250	-	41.0	-

It should also be noted that transmission oils have higher classification numbers than engine oils.

As can be seen from Figure 14, this does not mean that they are more viscous than the engine oils. The higher numbers simply make it easier to differentiate between engine and transmission oils.

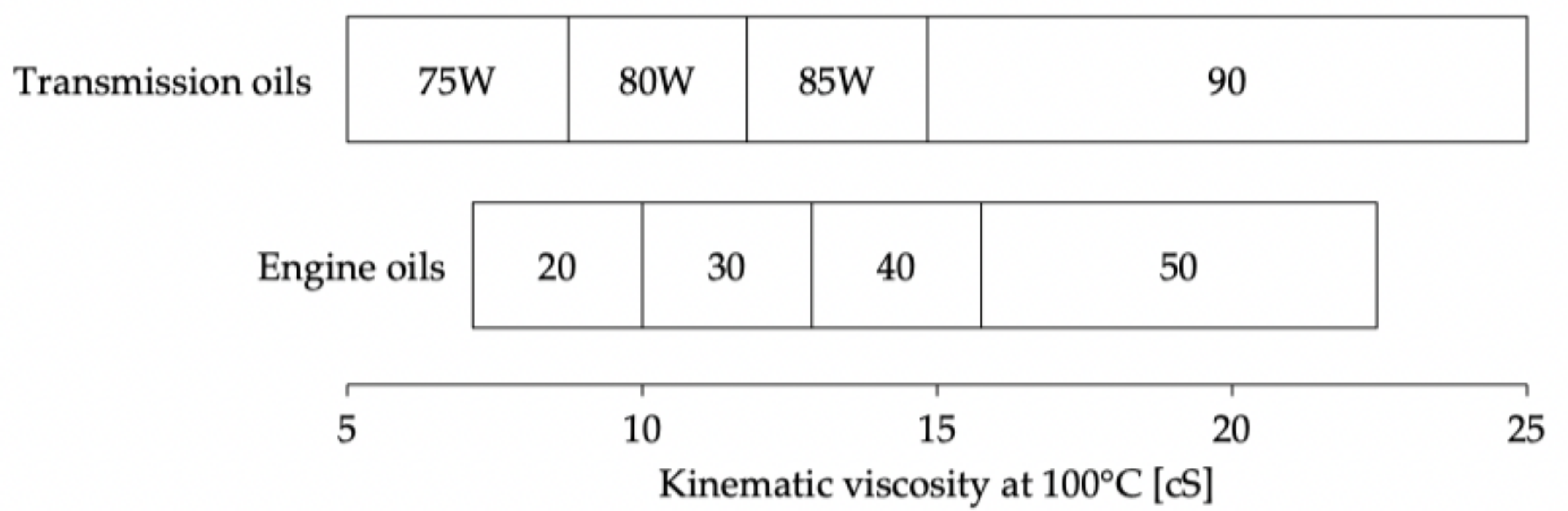


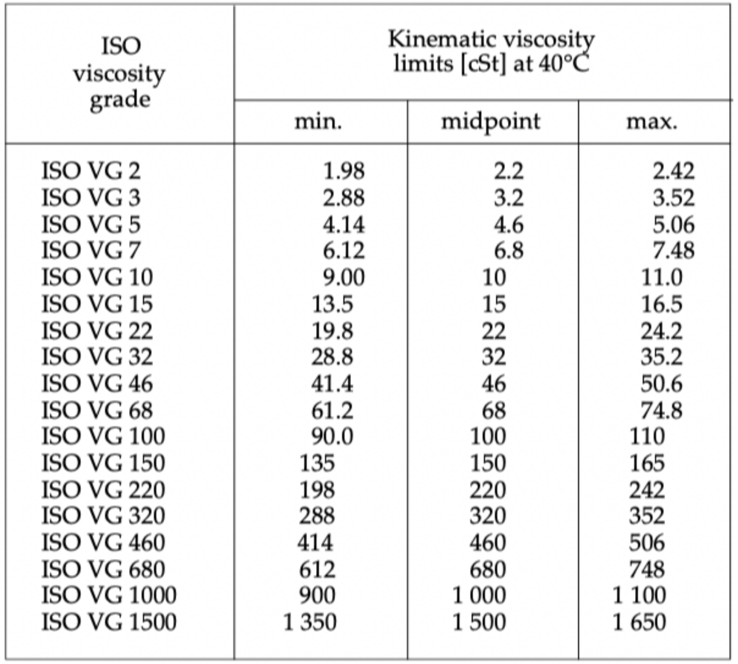
Figure 14: Comparison of SAE grades of engine and transmission oils.

ISO Viscosity classification

The ISO (International Standards Organization) viscosity classification system was developed in the USA by the American Society of Lubrication Engineers (ASLE) and in the United Kingdom by The British Standards Institution (BSI) for all industrial lubrication fluids.

It is now commonly used throughout industry. The industrial oil viscosities for different ISO viscosity grade numbers are shown in Table 6 (ISO 3448).

Table 6: ISO classification of industrial oils.



ISO viscosity grade	Kinematic viscosity limits [cSt] at 40°C		
	min.	midpoint	max.
ISO VG 2	1.98	2.2	2.42
ISO VG 3	2.88	3.2	3.52
ISO VG 5	4.14	4.6	5.06
ISO VG 7	6.12	6.8	7.48
ISO VG 10	9.00	10	11.0
ISO VG 15	13.5	15	16.5
ISO VG 22	19.8	22	24.2
ISO VG 32	28.8	32	35.2
ISO VG 46	41.4	46	50.6
ISO VG 68	61.2	68	74.8
ISO VG 100	90.0	100	110
ISO VG 150	135	150	165
ISO VG 220	198	220	242
ISO VG 320	288	320	352
ISO VG 460	414	460	506
ISO VG 680	612	680	748
ISO VG 1000	900	1 000	1 100
ISO VG 1500	1 350	1 500	1 650

Lubricant density and specific gravity

Lubricant density is important in engineering calculations and sometimes offers a simple way of identifying lubricants. Density or specific gravity is often used to characterize crude oils. It gives a rough idea of the amount of gasoline and kerosene present in the crude. The oil density, however, is often confused with specific gravity.

Specific gravity is defined as the ratio of the mass of a given volume of oil at temperature “t_1” to the mass of an equal volume of pure water at temperature “t_2” (ASTM D941, D1217, D1298).

For petroleum products, the specific gravity is usually quoted using the same temperature of 60°F (15.6°C). Density, on the other hand, is the mass per unit volume of oil (kg/m^3).

In the petroleum industry an API (American Petroleum Institute) unit is used which is a derivative of the conventional specific gravity. The API scale is expressed in degrees which in some cases are more convenient to use than specific gravity readings. The API specific gravity is defined as [23]:

$$\text{Degree API} = \left(\frac{141.5}{s}\right) - 131.5$$

s: Specific gravity at 15.6°C (60°F)

As mentioned already, the density of a typical mineral oil is about 850 (kg/m^3) and, since the density of water is about 1,000 (kg/m^3), the specific gravity of mineral oils is typically 0.85.

Thermal properties of lubricants

The most important thermal properties of lubricants are:
specific heat
thermal conductivity and
thermal diffusivity.

These three parameters are essential in assessing heating effects in lubrication, e.g., the cooling properties of the oil, the operating temperature of the surfaces, etc.

They are also important in bearing design.

Specific heat

Specific heat varies linearly with temperature and increases with increasing polarity or hydrogen bonding of the molecules.

The specific heat of an oil is usually half that of water.

For mineral and synthetic hydrocarbon-based lubricants, specific heat is in the range from about 1,800 (J/kg.K) at 0°C to about 3,300 (J/kgK) at 400°C.

Thermal conductivity

Thermal conductivity also varies linearly with temperature and is affected by polarity and hydrogen bonding of the molecules.

The thermal conductivity of most of the mineral and synthetic hydrocarbon based lubricants is in the range between 0.14 (W/mK) at 0°C and 0.11 (W/mK) at 400°C.

Thermal diffusivity

Thermal diffusivity is the parameter describing the temperature propagation into the solids.

Temperature characteristics of lubricants

The temperature characteristics are important in the selection of a lubricant for a specific application. In addition the temperature range over which the lubricant can be used is of extreme importance.

At high temperatures, oils decompose or degrade by thermal decomposition or oxidation, while at low temperatures oils may become near solid or even freeze.

During service, oils may release deposits and lacquers on contacting surfaces, form emulsions with water or produce a foam when vigorously churned. These effects are undesirable and have been the subject of intensive research.

The degradation of oil does not just affect the oil, but more importantly can lead to damage or failure of the lubricated contacts. It may also result in detrimental secondary effects to the operating machinery.

A prime example of secondary damage is corrosion caused by the acidity of oxidized oils. The most important temperature characteristics of a lubricant are:

pour point
flash point
volatility
oxidation and
thermal stability.

Pour point and cloud point

The pour point of an oil (ASTM D97, D2500) is the lowest temperature at which the oil will just flow when it is cooled.

In order to determine the pour point, the oil is first heated to ensure solution of all ingredients and elimination of any influence of past thermal treatment. It is then cooled at a specific rate and, at decrements of 3°C, the container is tilted to check for any movement.

The temperature 3°C above the point at which the oil stops moving is recorded as the pour point.

This oil property is important in the lubrication of any system exposed to low temperature, such as automotive engines, construction machines, military and space applications. When oil ceases to flow this indicates that sufficient wax crystallization has occurred or that the oil has reached a highly viscous state.

At this stage waxes or high molecular weight paraffins precipitate from the oil. The waxes form the interlocking crystals that prevent the remaining oil from flowing. This is a critical point since the successful operation of a machine depends on the continuous supply of oil to the moving parts.

The viscosity of the oil at the pour point is usually very large, i.e., several hundred (Pa.s), but the exact value is of little practical significance since what is important is the minimum temperature at which the oil can be used.

The cloud point is the temperature at which paraffin wax and other materials begin to precipitate. The onset of wax precipitation causes a distinct cloudiness or haze visible in the bottom of a jar of oil. This phenomenon has some practical applications in capillary or wick fed systems in which the wax formed may obstruct the oil flow. It is limited only to transparent fluids since measurement is based purely on observation.

If the cloud point of an oil is observed at a temperature higher than the pour point, the oil is said to have a “Wax Pour Point”.

If the pour point is reached without a cloud point the oil shows a simple “Viscosity Pour Point”.

There is also another critical temperature known as the “Flock Point”, which is primarily limited to refrigerator oils. It is the temperature at which the oil separates from the mixture, which consists of 90% refrigerant and 10% oil. The Flock point provides an indication of how the oil reacts with a refrigerant, such as Freon, at low temperature.

Flash point and fire point

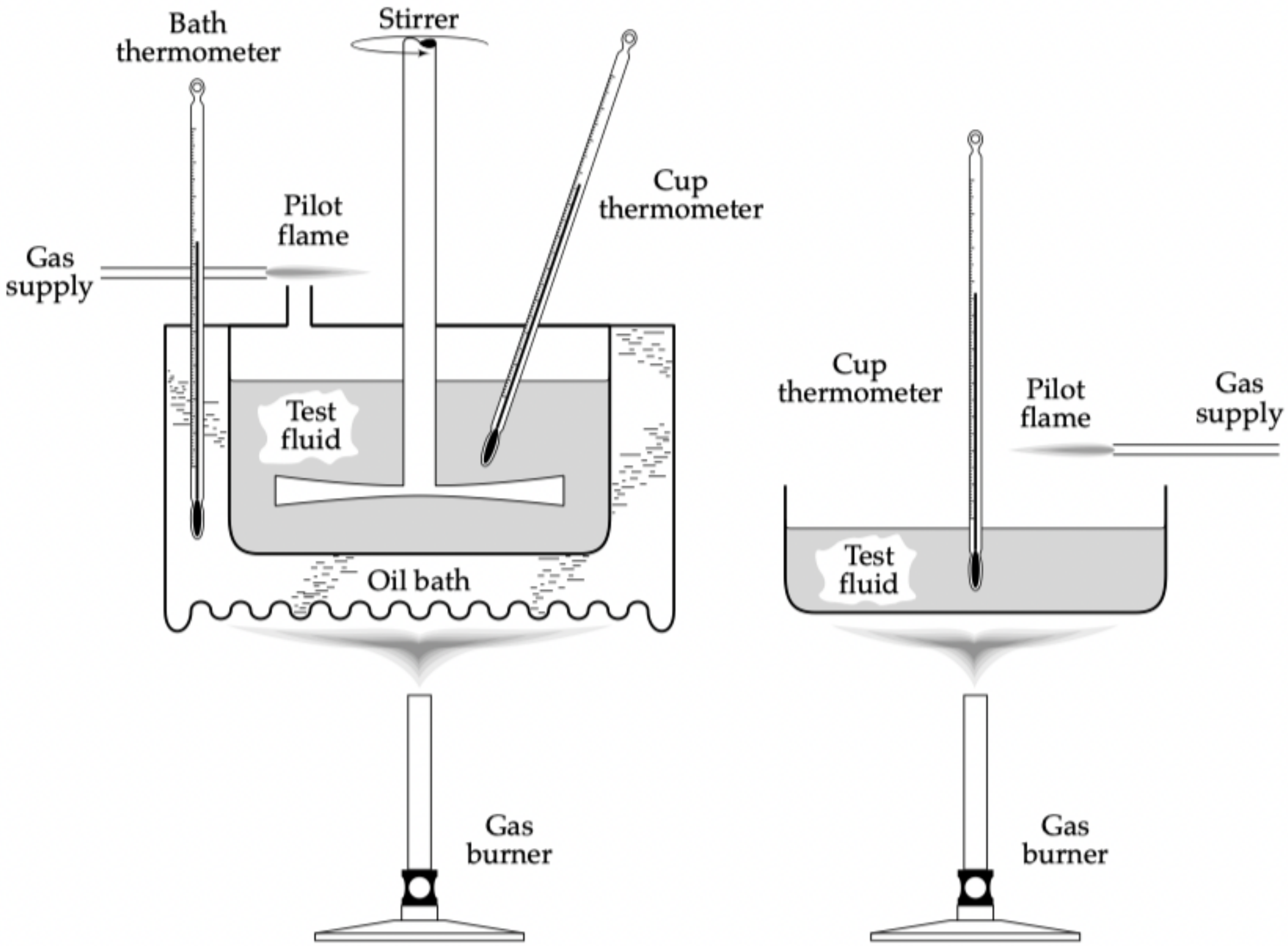
The “flash point” of the lubricant is the temperature at which its vapor will ignite.

In order to determine the flash point the oil is heated at a standard pressure to a temperature which is just high enough to produce sufficient vapor to form an ignitable mixture with air. This is the flash point.

The “fire point” of an oil is the temperature at which enough vapor is produced to sustain burning after ignition. The schematic diagram of a flash and fire point apparatus is shown in Figure 15.

Flash and fire points (ASTM D92, D93, D56, D1310) are very important from a safety view point since they constitute the only factors that define the fire hazard of a lubricant.

In general, the flash point and fire point of oils increase with increasing molecular weight. For a typical lubricating oil, the flash point is about 210°C whereas the fire point is about 230°C.



Closed-cup test apparatus

Open-cup test apparatus

Figure 15: Schematic diagram of the flash and fire point apparatus.

Volatility and evaporation

In many applications the loss of lubricant due to evaporation can be significant. The temperature has a controlling influence on evaporation. At elevated temperatures in particular, oils may become more viscous and greases tend to stiffen and eventually dry out because of evaporation.

Volatile components of the lubricant may be lost through evaporation, resulting in a significant increase in viscosity and a further temperature rise due to higher friction, which in turn causes further oil losses due to evaporation.

Volatility of lubricants is expressed as a direct measure of evaporation losses (ASTM D2715).

In order to determine the lubricant volatility, a known quantity of lubricant is exposed in a vacuum thermal balance device. The evaporated material is collected on a condensing surface and the decreasing weight of the original material is expressed as a function of time.

Depending on available equipment it is possible to obtain quantitative evaporation data together with some information on the identity of the volatile products. Frequently the evaporation rates are determined at various temperatures. A schematic diagram of an evaporation test apparatus is shown in Figure 16.

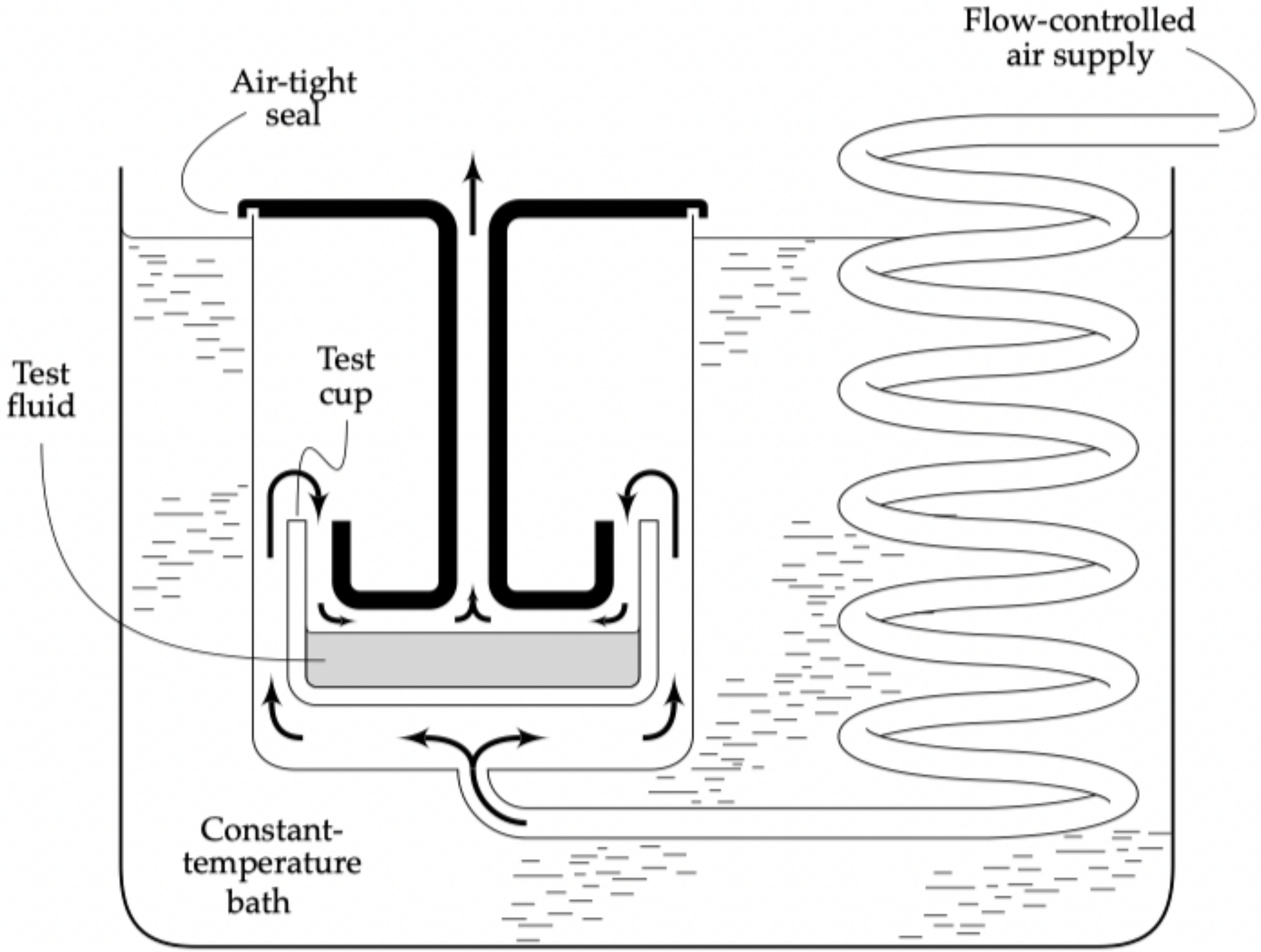


Figure 16: Schematic diagram of the evaporation test apparatus.

In this device a known quantity of oil is placed in a specially designed cup. The air enters the periphery of the cup and flows across the surface of the sample and exits through the centrally located tube.

Prior to the test the cell is preheated to the required temperature in an oil bath. The flow rate of air is about 2 (litres/min).

The cup is aerated for 22 hours then cooled and weighed at the end of the test.

The percentage of lost mass gives the evaporation rate.

Oxidation stability

Oxidation stability (ASTM D943, D2272, D2893, D1313, D2446) is the resistance of a lubricant to molecular breakdown or rearrangement at elevated temperatures in the ordinary air environment.

Lubricating oils can oxidize when exposed to air, particularly at elevated temperatures, and this has a very strong influence on the life of the oil. The rate of oxidation depends on the degree of oil refinement, temperature, presence of metal catalysts and operating conditions. It increases with temperature.

Oxidation of oils is a complex process as different compounds are generated at different temperatures.

For example, at about 150°C organic acids are produced whereas at higher temperatures aldehydes are formed.

The oxidation rates vary between different compounds, as shown in Table 7.

Table 7: Oxidation rates for common compounds.

Paraffins	Most resistant
Naphthenes	⇕
Aromatics	
Asphaltenes	
Unsaturates	Least resistant

One way of improving oxidation stability is to remove the hydrocarbon-type aromatics and molecules containing sulphur, oxygen, nitrogen, etc.

This is achieved through refining. More refined oil has better oxidation stability. It is also more expensive and has poorer boundary lubrication characteristics, so oil selection for a particular application is always a compromise, depending on the type of job the oil is expected to perform.

Oxidation can also be controlled by additives that attack the hyperoxides formed in the initial stages of oxidation or break the chain reaction mechanism by scavenging free radicals. The products of oxidation usually consist of acidic compounds, sludge and lacquers. All of these compounds cause oil to become more corrosive, more viscous and also cause the deposition of insoluble products on working surfaces, restricting the flow of oil in operating machinery. This interferes with the performance of the machinery.

Oxidation stability is a very important oil characteristic, especially where extended life is required, e.g., turbines, transformers, hydraulic and heat transfer units, etc.

A lubricant with limited oxidation stability requires more frequent maintenance or replacement, resulting in higher operating costs. Under more severe conditions the oil changes may need to take place more frequently, hence the operating costs will be even higher.

Many tests have been devised to assess the oxidation characteristics of oils and there is no clear rationale for selecting a particular test. Some have been devised for specific applications, for example, the assessment of oxidation characteristics of railway diesel engine lubricants.

In most test apparatus, the oil is in contact with selected catalysts and is exposed to air or oxygen, and the effects are measured in terms of acid or sludge formed, viscosity change, etc. A schematic diagram of a typical oxidation apparatus is shown in Figure 17.

In this apparatus oxygen is passed through the oil sample placed in the reaction vessel. The reaction vessel consists of a large test tube with a smaller central removable oxygen inlet tube which supports the steel-copper catalyst coil. At the end of the tube there is a water-cooled condenser which returns the more volatile components to the reaction.

About 300 (ml) of oil together with 60 (ml) of distilled water is placed in the test tube. The flow rate of oxygen is about 0.5 (litre/min) and the test is conducted at a temperature of 95°C.

During the test acidic compounds are produced in the tube, and the neutralization number determined at the end of the test is a measure of the oxidation stability of the oil. The tests are usually run over a specific period of time.

For example, Differential Scanning Calorimetry has been employed to assess oxidation stability of oils.

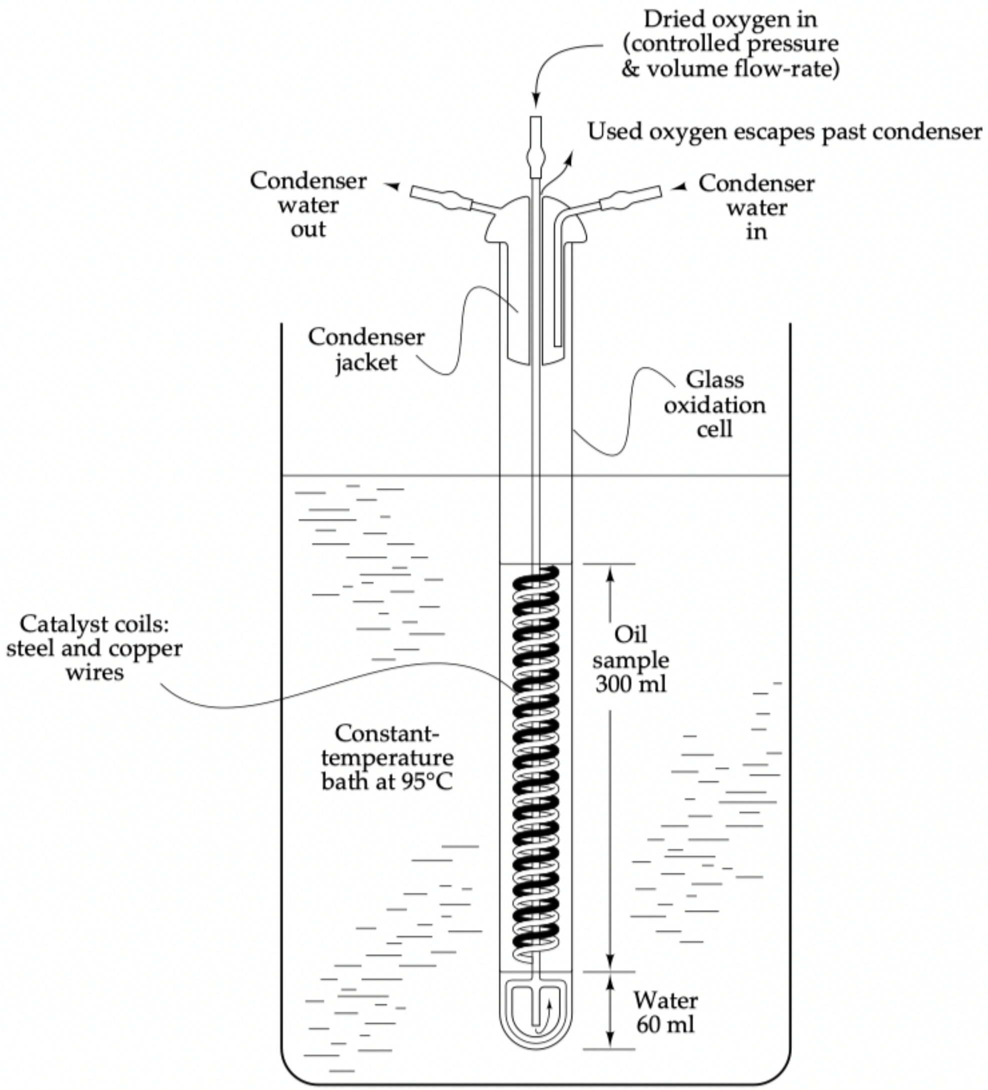


Figure 17: Schematic diagram of an oxidation test apparatus.

Thermal stability

When heated above a certain temperature oils will start to decompose, even if no oxygen is present.

Thermal stability is the resistance of the lubricant to molecular breakdown or molecular rearrangement at elevated temperatures in the absence of oxygen. When heated, mineral oils break down to methane, ethane and ethylene.

Thermal stability can be improved by the refining process, but not by additives.

It can be measured by placing the oil in a closed vessel with a manometer monitoring the rate of pressure increase when the container is heated at a specific rate under nitrogen atmosphere. Mineral oils with a substantial percentage of C-C single bonds have a thermal stability limit of about 350°C.

Synthetic oils, in general, exhibit better thermal stability than mineral oils. However, there can be exceptions. For example, synthetic hydrocarbons produced by the polymerization or oligomerization process, although possessing the same basic structures as mineral oils, have a thermal stability limit 28°C or more below that of mineral oils.

Lubricants with aromatic linkages or with aromatic linkages and methyl groups as side chains exhibit a thermal stability limit of about 460°C. The additives used for lubrication improvement usually have a thermal stability below that of base oils.

In general, thermal degradation of the oil takes place at much higher temperatures than oxidation. Thus the maximum temperature at which an oil can be used is determined by its oxidation stability.

In Figures 18 and 19 the relationships between lubricant life and temperature are shown for mineral and synthetic oils, respectively.

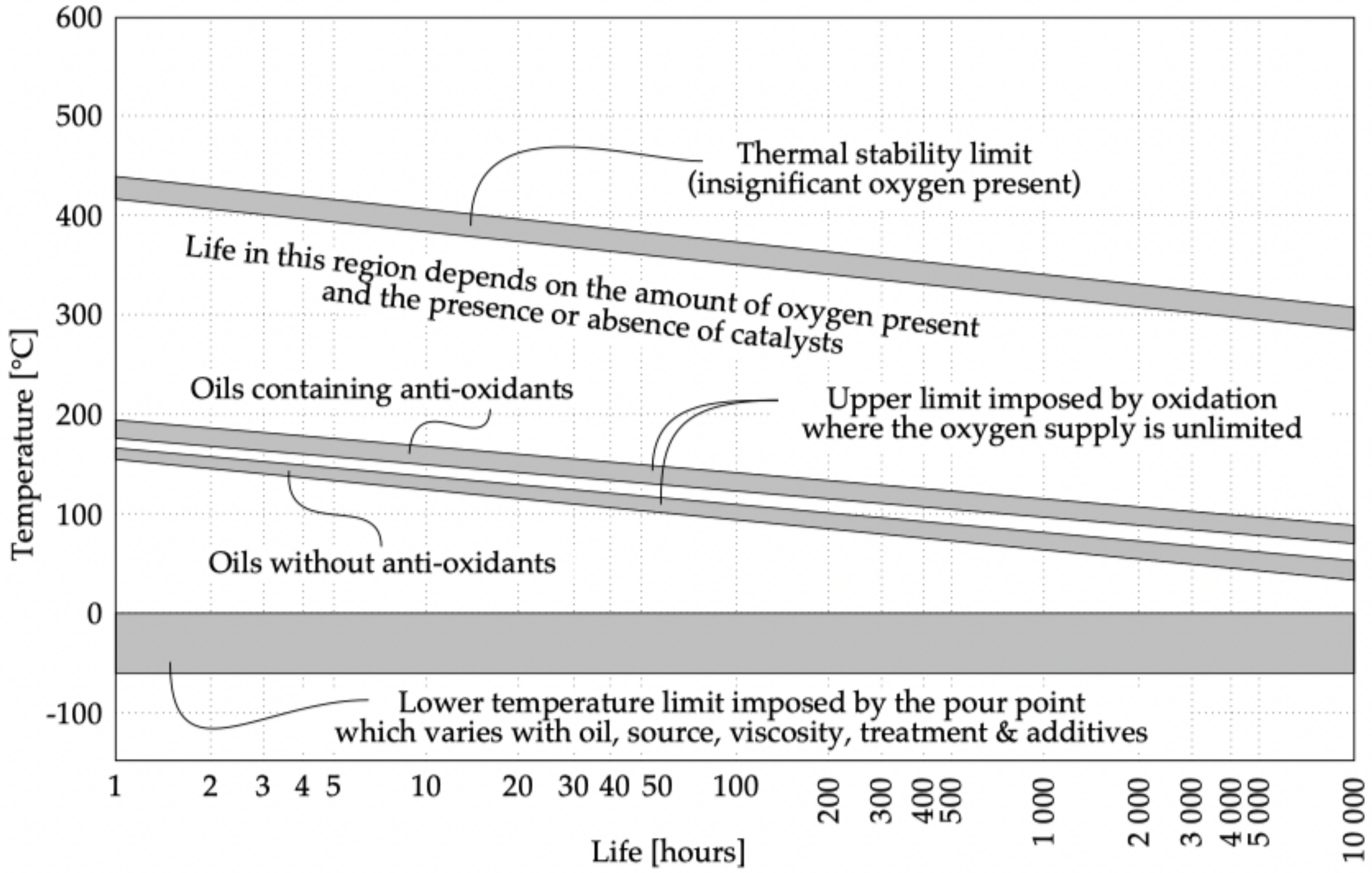


Figure 18: Temperature-life limits for mineral oils.

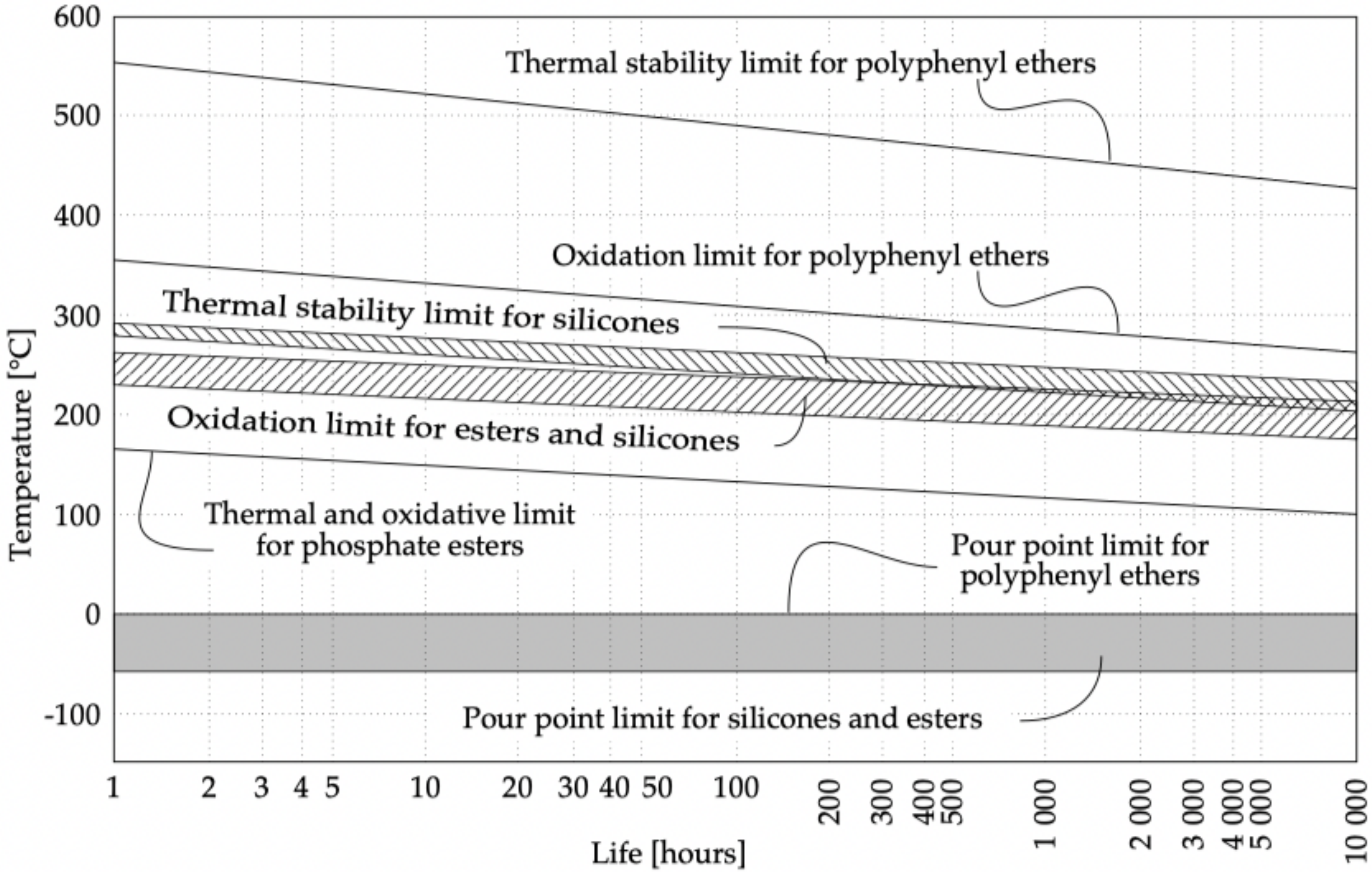


Figure 19: Temperature-life limits for selected synthetic oils.

Other lubricant characteristics

There are many other lubricant characteristics described in the literature and the most frequently used include:

surface tension
neutralization number and
carbon residue.

Surface tension

Various lubricants generally show some differences in the degree of wetting and spreading on surfaces. Furthermore, the same lubricant can show different wetting and spreading characteristics depending on the degree of oxidation or on the modification of the lubricant by additives.

The phenomena of wetting and spreading are dependent on surface tension (ASTM D971, D2285), which is especially sensitive to additives, e.g., less than 0.1 wt% of silicone in mineral oil will reduce the surface tension of the oil to that of silicone.

Surface and interfacial tension are related to the free energy of the surface, and the attraction between the surface molecules is responsible for these phenomena. Surface tension refers to the free energy at a gas-liquid interface, while interfacial tension takes place at the interface between two immiscible liquids.

Surface tension can be measured by the “du Noy ring method” (ASTM D971). A schematic diagram of surface tension measurement principles is shown in Figure 20. It involves the measurement of the force necessary to detach the platinum wire ring from the surface of the liquid. The surface tension is then calculated from the following formula:

$$\sigma_s = \frac{F}{4\pi r}$$

σ_s:Surface tension in N/m
F:Force in Newton
r:Radius of the platinum ring in meter

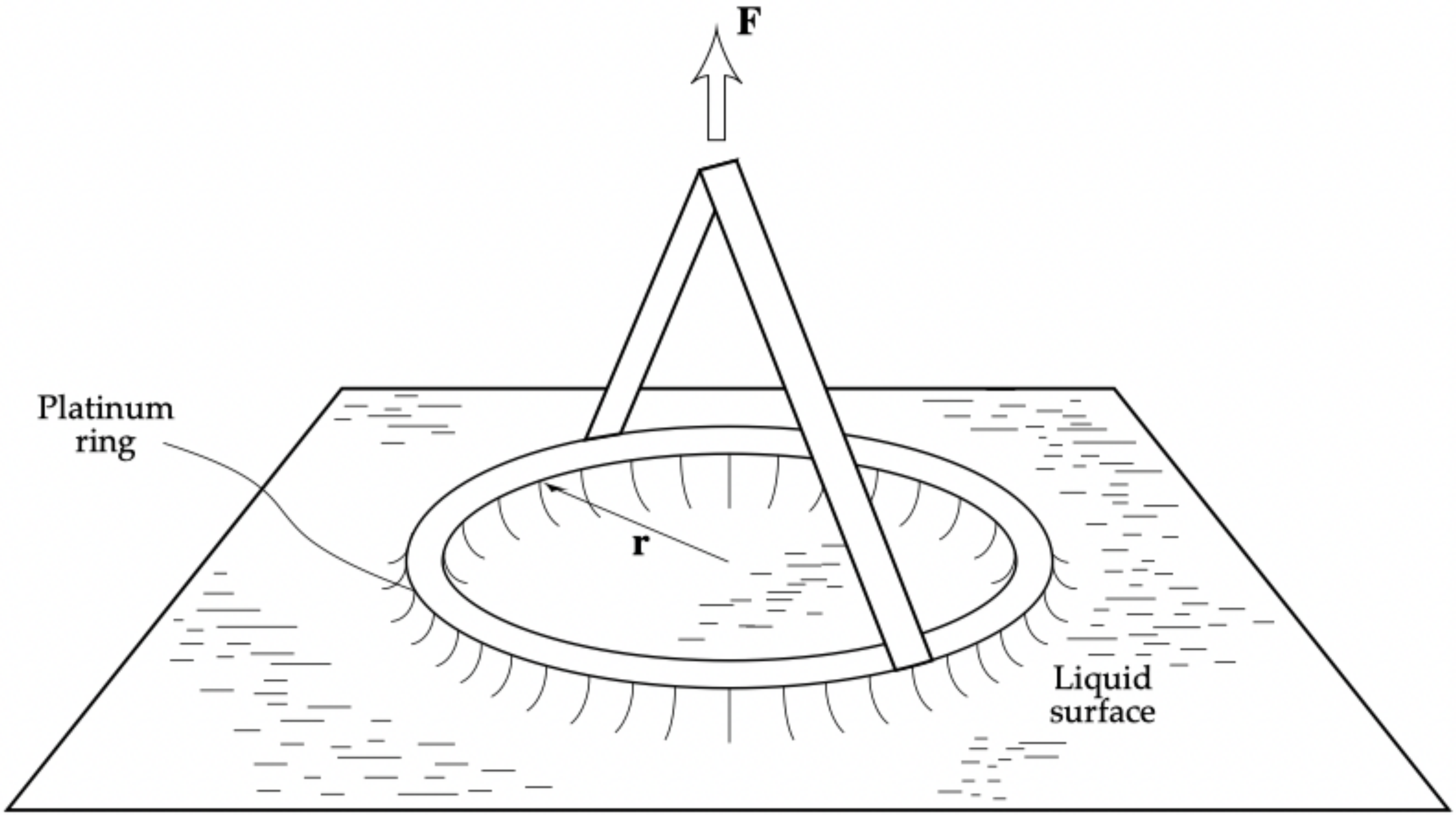
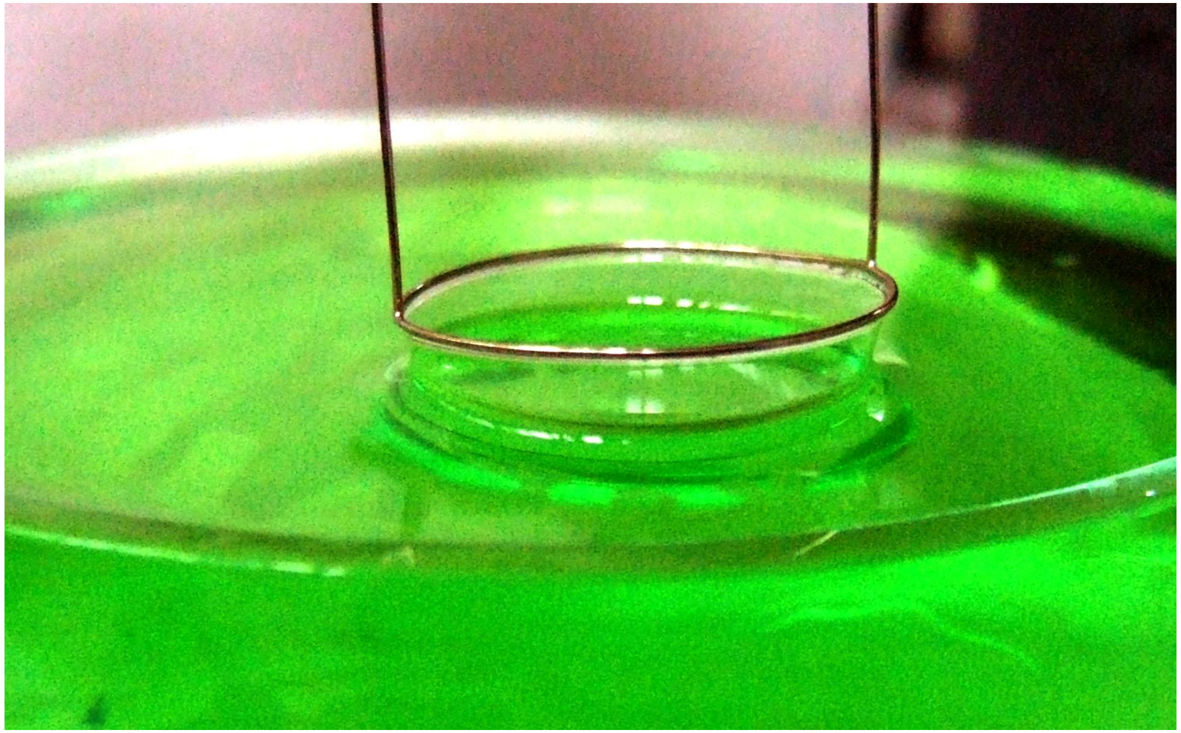


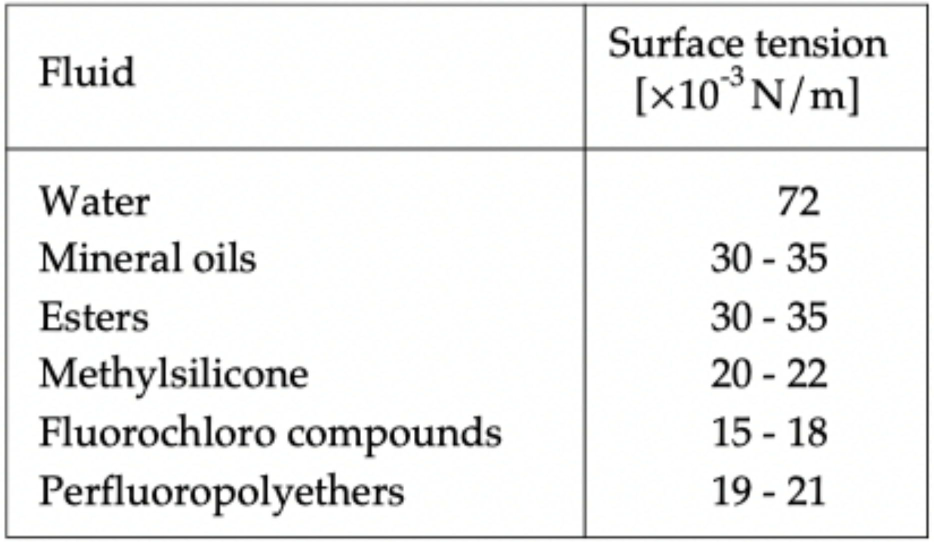
Figure 20: Schematic diagram of surface tension measurement principles.

Real image of the “du Noy ring method”.



Typical values of surface tension for some basic fluids are shown in Table 8. Surface tension is frequently used together with the neutralization number as a measure of oil deterioration in transformers, hydraulic systems and turbines. Interfacial tension between two immiscible liquids is approximately equal to the difference in the surface tension between the two liquids.

Table 8: Surface tension of some basic fluids.



Fluid	Surface tension $[\times 10^{-3}\,\mathrm{N/m}]$
Water	72
Mineral oils	30 - 35
Esters	30 - 35
Methylsilicone	20 - 22
Fluorochloro compounds	15 - 18
Perfluoropolyethers	19 - 21

Neutralization number

The neutralization number of a lubricant (ASTM D974, D664) is the quantity in milligrams of potassium hydroxide (KOH) per gram of oil necessary to neutralize acidic or alkaline compounds present in the lubricant.

The procedure described in D664 is the most popular method for determining the acidic condition of the oil. The results are reported as a Total Acid Number (TAN) for acidic oils and as a Total Base Number (TBN) for alkaline oils.

TAN is expressed as the amount of potassium hydroxide in milligrams necessary to neutralize 1 gram of oil.

TBN is the amount of potassium hydroxide in milligrams necessary to neutralize the hydrochloric acid (HCl) which would be required to remove the basicity in 1 gram of oil.

So, the TAN is a measure of acidic matter remaining in the oil and the TBN is the measure of alkaline matter remaining in the oil.

In general, TBN applies only to the oil supplied with alkaline additives to suppress sulphur-based acid formation in the presence of low-grade fuels such as diesel engine lubricants. Thus TBN is a negative measure of oil acidity and a minimum value should be maintained.

On the other hand, the TAN number applies to most oils since they are normally weakly acidic. During the test, the neutralizing solution is added until all acid or alkaline ingredients are neutralized.

The neutralization number is useful in assessing changes in the lubricant that occur during service under oxidizing conditions. It is frequently used in conjunction with the other parameters, such as interfacial tension, in lubricant condition monitoring.

The best test results are achieved in systems which are relatively free of contaminants such as steam turbine generators, transformers, hydraulic systems, etc. It can also be used in the condition monitoring of oils operating in engines, compressors, gears and as cutting fluids. Usually a limiting neutralization number is established as a criterion indicating when oil needs to be changed or reclaimed.

Carbon residue

At temperatures of 300°C or more in the absence of air, oils may decompose to produce low molecular weight fragments from the large molecular weight species typically found in mineral oils.

The fragmented or “cracked” hydrocarbon molecules either recombine to form tarry deposits (asphaltenes) or are released to the atmosphere as volatile components.

The deposits are undesirable in almost all cases and most lubricating oils are tested for deposit forming tendencies. The carbon residue (ASTM D189, D524) is determined by weighing the residue after the oil has been heated to a high temperature in the absence of air.

The carbon residue parameter is of little importance in the case of synthetic oils because of their good thermal stability.

It is also infrequently used in characterizing well refined lubricants.

Optical properties of lubricants

Refractive index

The refractive index (ASTM D1218, D1747) is defined as the ratio of the velocity of a specified wavelength of light in air to that in the oil under test and it can be measured by an Abbe refractometer.

It is a function of temperature and pressure. The refractive index of very viscous lubricants is measured at temperatures between 80°C and 100°C and of typical oils at 20°C.

Refractive index is sensitive to oil composition and hence it is useful in characterizing base stocks.

It is very important in calculations of minimum film thickness in experiments involving optical interferometry.

For most mineral oils, the value of the refractive index at atmospheric pressure is about 1.51 (It is dimensionless).

Additive compatibility and solubility

Additives used in lubricants should be compatible with each other and soluble in the lubricant. These additive features are defined as additive compatibility and additive solubility.

Additive compatibility

Two or more additives in an oil are compatible if they do not react with each other and if their individual properties are beneficial to the functioning of the system. It is usually considered that additives are compatible if they do not give visible evidence of reacting together, such as a change in colour or smell. This also refers to the compatibility of two or more finished lubricants.

Lubricants should also be compatible with the component materials used in a specific application. For example, mineral oils are incompatible with natural rubber, and phosphate esters are incompatible with many different rubbers. Mineral oils give very poor performance with red hot steels because they produce carburization while rapeseed oil does not have this problem.

In most industries these problems can be overcome by careful selection of lubricants. On the other hand, in some industries, such as pharmaceutical and food processing where oil leaks are unacceptable, process fluids might be used as lubricants. For example, in sugar refining high viscosity syrups and molasses can be used, if necessary, to lubricate the bearings, but they are in general poor lubricants and their use may lead to severe equipment or machinery problems.

Additive solubility

The additive must dissolve well in petroleum products.

It must remain dissolved over the entire operating temperature range.

Separation of an additive in storage or in service is highly undesirable. For example, elemental sulphur could be used as an additive in extreme conditions of temperature and pressure but it is insoluble in oil under atmospheric conditions and would separate during storage and service.

Lubricant impurities and contaminants

Water content

Water content (ASTM D95, D1744, D1533, D96) is the amount of water present in the lubricant. It can be expressed as parts per million, percent by volume or percent by weight.

It can be measured by centrifuging, distillation and voltametry. The most popular, although least accurate, method of water content assessment is the centrifuge test. In this method a 50% mixture of oil and solvent is centrifuged at a specified speed until the volumes of water and sediment observed are stable.

Apart from water, solids and other soluble are also separated and the results obtained do not correlate well with those obtained by the other two methods.

The distillation method is a little more accurate and involves distillation of oil mixed with xylene. Any water present in the sample condenses in a graduated receiver.

The voltametry method is the most accurate. It employs electrometric titration, giving the water concentration in parts per million.

Corrosion and oxidation behavior of lubricants is critically related to water content.

An oil mixed with water gives an emulsion. An emulsion has a much lower load carrying capacity than pure oil and lubricant failure followed by damage to the operating surfaces can result.

In general, in applications such as turbine oil systems, the limit on water content is 0.2% and for hydraulic systems 0.1%.

In dielectric systems excessive water content has a significant effect on dielectric breakdown. Usually the water content in such systems should be kept below 35 (ppm).

Sulphur content

Sulphur content (ASTM D1266, D129, D1662) is the amount of sulphur present in an oil.

It can have some beneficial, as well as some detrimental, effects on operating machinery.

Sulphur is a very good boundary agent, which can effectively operate under extreme conditions of pressure and temperature. On the other hand, it is very corrosive.

A commonly used technique for the determination of sulphur content is the bomb oxidation technique. It involves the ignition and combustion of a small oil sample under pressurised oxygen. The sulphur from the products of combustion is extracted and weighed.

Ash content

There is some quantity of non-combustible material present in a lubricant which can be determined by measuring the amount of ash remaining after combustion of the oil (ASTM D482, D874).

The contaminants may be wear products, solid decomposition products from a fuel or lubricant, atmospheric dust entering through a filter, etc.

Some of these contaminants are removed by an oil filter but some settle into the oil. To determine the amount of contaminant, the oil sample is burned in a specially designed vessel.

The residue that remains is then ashes in a high-temperature muffle furnace and the result displayed as a percentage of the original sample.

The ash content is used as a means of monitoring oils for undesirable impurities and sometimes additives. In used oils it can also indicate contaminants such as dirt, wear products, etc.

Chlorine content

The amount of chlorine in a lubricant should be at an optimum level.

Excess chlorine causes corrosion whereas an insufficient amount of chlorine may cause wear and frictional losses to increase.

Chlorine content (ASTM D808, D1317) can be determined either by a bomb test which provides the gravimetric evaluation or by a volumetric test which gives chlorine content, after reacting with sodium metal to produce sodium chloride, then titrating with silver nitride.

Solubility of gases in oils

Almost all gases are soluble in oil to a certain extent. Oxygen dissolved in oil affects friction and wear of metal surfaces.

Bubbles of gas (usually air) which are released in the oil of hydraulic systems due to the drop in pressure may cause a drastic increase in the compressibility of the hydraulic fluid, affecting the overall performance of the system.

The solubility of a gas in a liquid is calculated from the Ostwald coefficient, which is defined as the ratio of the volume of dissolved gas to the volume of solvent liquid at the test temperature and pressure.

For example, if the Ostwald coefficient is equal to 0.2 then 5 litres of oil will contain $0.2 \times 5 = 1$ litre of dissolved gas.

The solubility of a gas in a liquid is usually proportional to pressure, so that the Ostwald coefficient, defined in terms of the volume of gas, remains constant. On the other hand, to define this coefficient in terms of mass would require the introduction of a pressure proportionality parameter. Hence the coefficient defined in terms of volume of gas is commonly used. The formulae necessary for the evaluation of the Ostwald coefficient (ASTM D2779) are empirical.

One of the serious limitations of the method above is that it applies only to mineral oils.

A more general formula based on a combination of linear regression of experimental results and detailed application of solvation theory has been developed by Beerbower. However, Beerbower introduced two new parameters in the formula.