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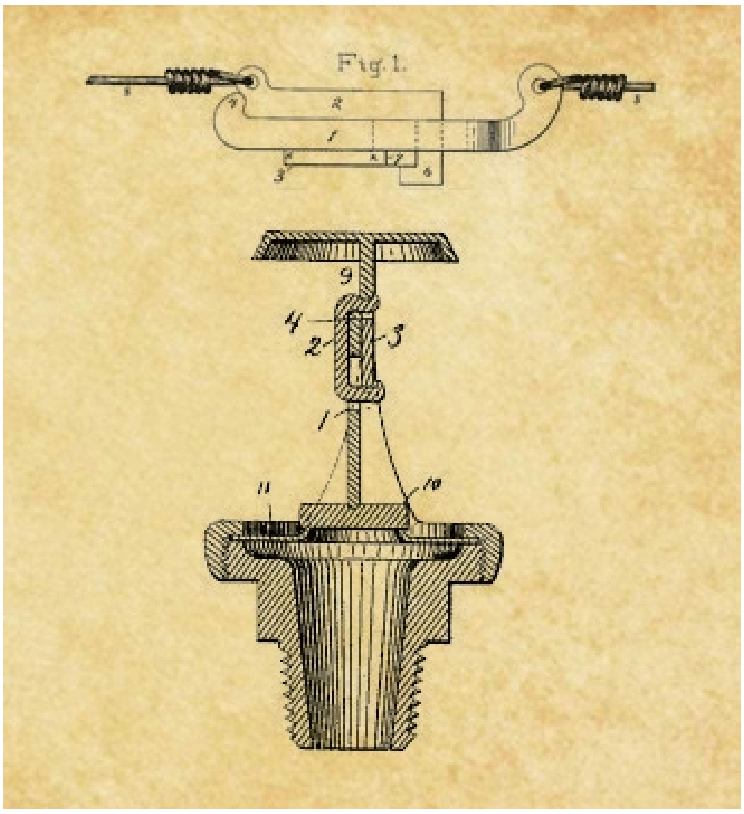
English version

ULTIMHEAT® MUSEUM

History of technologies linked to heating.

Chapter 3

Historical introduction on fusible alloys



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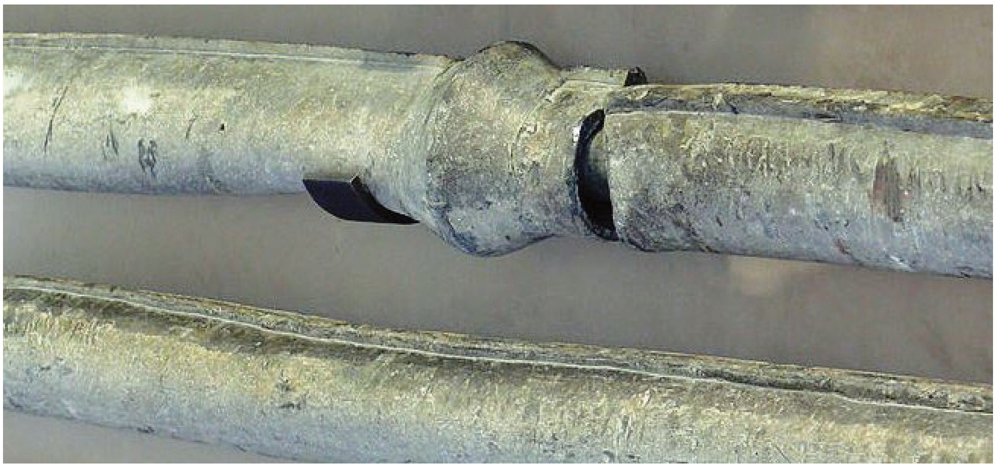
The history of low temperature fusible alloys is a succession of stages, spread over two millennia, according to the successive discoveries of metals



Roman waterpipe, made of soldered lead strips (Museum of Arles et de la Provence antique (extraite de https://commons.wikimedia.org/w/index.php?curid=10214375)

and experiments.

The 183°C limit: The binary alloys of lead and tin

The earliest known piece made of lead and tin alloy seems to be an Egyptian vase found in Abydos, dated around 1400 BC.

During the Roman Empire, lead was used for the construction of water pipes. Melting at 325°C, it was easily melted into strips. As it does not self-weld, it was a mixture of lead and tin that was used to weld the strips rolled together into hoses. Although they did not have temperature measuring devices, the Romans had noticed that by adding a certain percentage of tin (melting at 235°C) imported from Cornwall to the lead, the mixture melted at a temperature less than that of lead. In his Natural History, Pliny the Elder, in the course of the first century, gave the formula for welding the lead tubes: two parts of lead for a part of tin. (Melting range of the alloy 66.7-33.3: 185-250°C).

Alloys with 4 parts of lead and one part of tin (melting range for the 80-20 alloy: 183-275°C) and 5 parts of lead and one part of tin (melting range of the alloy 83.3-16.7: 225-290°C) are then given for a temperature of 81.3.3 / 4 according to the Isaac Newton scale in 1701.

Still in the middle of the 18th century, this anomaly in the alloys always intrigued and remained unexplained "One thing that is still rather singular; it is because any two metals mixed together are melted at a lower fire than if they were separated. " (Dissertation on the nature and propagation of fire, by the Marquise Du Chatelet, 1744)

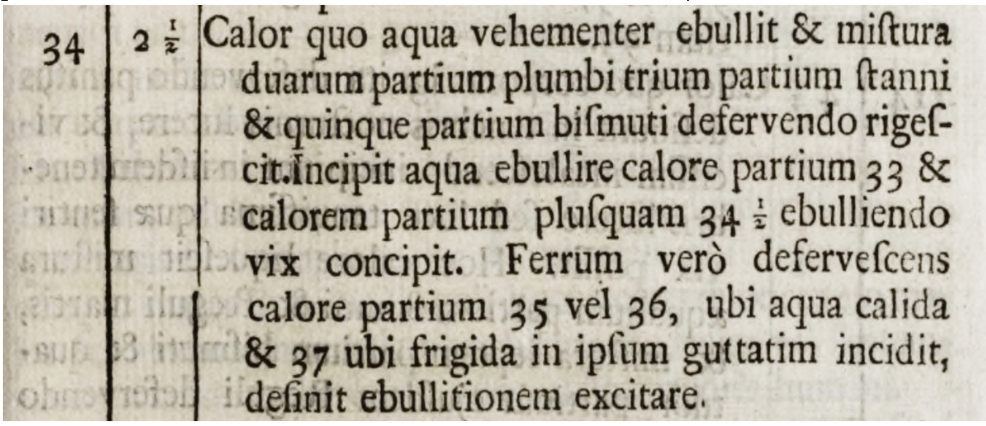
In the 18th century, tinsmiths used a solder with 50% lead and 50% tin (melting range 183-216°C). For tin potters it was still not enough because too close to the melting temperature of the tin. It is likely that it was the Cornish tin potters who found the binary alloy with the lowest melting point, made of 63% tin and 37% lead (3 parts of lead and 5 parts of tin). At the beginning of the 18th century this eutectic alloy melting at 183°C was commonly used for tinning copper kitchen vessels. Nowadays is still used as a welding alloy in the industry.

The 96°C limit: The Bismuth

It seems that the ancient Egyptians used bismuth oxide as a component of makeup and cosmetics "The White of Egypt". In 1413, Basil Valentine recorded it for the first time in the following terms: "Antimony is the bastard of lead, just as wismulh, or marcasite, is the bastard of tin". In a treatise of Agricola dating from the beginning of the 16th century (1529) it is described as being well known in

Germany and considered as a particular metal. Others considered it a kind of lead. Bismuth was later extensively described in Moyse Charas's "Royal Galenic and Chymyque Royal Pharmacopoeia" in 1676, but its extraction and purification from tin or copper ores was complex.

The miners of the time considered bismuth as silver not yet completely transmuted and named its ore "Argenti tectum" (M. Hellot, Memoirs of the French Academy, 1737, p 231) In 1701, the first low-temperature ternary alloys using bismuth tin and lead were described by Isaac Newton in his article "Scalum graduum Caloris" (Philosophical Transactions, 1701, 270, P824-82) to serve as a reference point for thermometer calibrations. In this article in Latin, he described in particular an alloy consisting of 2 parts of lead (20%), 3 parts of tin (30%) and 5 parts of Bismuth (50%). This alloy is the one he considered to have the lowest melting point. He gave its temperature (graduated 34 1/2 in its scale) as being slightly higher than that of boiling water. (An alloy of this composition made with current pure metals is characterized by a liquidus temperature at 123°C and solidus at 96°C). He explored other ternary alloys of the same type, and also tin bismuth binary alloys. At that time, tin ore founders in the province of Cornwall used bismuth to make their tin shiny, hard and sonorous.



34 | $2\frac{1}{2}$ | Calor quo aqua vehementer ebullit & miſtura duarum partium plumbi trium partium ſtanni & quinque partium biſmuti deſervendo rigeſcit. Incipit aqua ebullire calore partium 33 & calorem partium pluſquam $34\frac{1}{2}$ ebulliendo vix concipit. Ferrum verò deferveſcens calore partium 35 vel 36, ubi aqua calida & 37 ubi frigida in ipſum guttatim incidit, deſinit ebullitionem excitare.

1701 description d'un alliage comportant 2 parties de plomb, 3 parties d'étain et cinq parties de bismuth par Isaac Newton dans « Scalum graduum caloris »

Studied empirically from the second half of the 18th century, the composition of these alloys varied as the development of increasingly pure metals.

In the second half of the eighteenth century, tin potters used many different types of welding, more or less secret, composed of lead, tin and bismuth (article "soudure"of the Encyclopédie, ou Dictionnaire raisonné des sciences, des arts et des métiers, 1775)

In 1753, the French scientist Claude Geoffroy The Young devoted himself to the study of Bismuth, which he described as a new metal and no longer as a semi-metal close to lead as it was previously considered. He died unfortunately before finishing his work. During his life, the German pharmacist Valentin Rose the Elder (1736-1771), studied different compositions of Bismuth, lead, tin alloys with low melting point of variable composition, which were only posthumously published in 1772. He left his name to one of them. In 1775, the French chemist Jean d'Arcet provided the Academy of Sciences with a report of his experiments on fusible alloys of lead, bismuth and tin, which had the particularity of melting in boiling water. They differed from previous alloys whose melting points (liquidus) were always higher than 100°C and only solidification (solidus) was below the boiling water. He described a set of more than ten compositional variations that were then known as D'Arcet or Darcet's Alloys. It was not until 1898 that the French chemist Georges Charpy revealed that there was only one eutectic point at 96°C for these ternary alloys, for a combination by weight of 52% Bismuth, 32% lead , and 16% tin. ("On the constitution of eutectic alloys, G. Charpy"). Many compositional variations close to this eutectic gave melting points approaching a few degrees, with a more or less extensive pasty zone, and could not therefore be considered as eutectic alloys.

The first application of one of these alloys melting at 98°C, consisting of three

parts of tin, eight parts of bismuth and five parts of lead, were anatomical injections, and the manufacture of stereotyped printing plates.
Some of these ternary alloys of bismuth, tin and lead, took the name of their inventors:
• The Rose's alloy (50% bismuth, 25-28% lead and 22-25% tin, with a melting point between 94°C and 98°C).
• The Newton's alloy, with a melting point at 95°C, comprising 50% of bismuth, 31% of lead and 19% of tin (NB:This composition does not correspond to its description of 1701).
• The Lichtenberg's alloy, melting at 92°C, contains 50% bismuth, 30% lead and 20% tin.
• The Malotte's metal melting at 95°C (203°F) contains 46% bismuth, 20% lead and 34% tin.
• The Homberg's alloy, melting at 121°C, contains 3 parts of lead, 3 of tin and 3 of bismuth.
In 1802 the British Richard Trevithick and Andrew Vivian invented the first high-pressure steam engine that opened the way for locomotives, the first of which was used in February 1804. In this vehicle, a fuse plug in lead in the bottom of the boiler served as a temperature safety device, and its melting was supposed to send a jet of steam, extinguishing the hearth below. A second plug, made of lower temperature fusible alloy, and located at the top of the boiler, in contact with the steam was supposed to melt when the temperature of it became too high. Although quickly considered unreliable and usable only as an auxiliary safety device, fusing plugs and fusible washers quickly became mandatory on steam engines: as of October 29, 1813, a decree of the French government forced the steam engine manufacturers, in addition to the safety valves, to apply a fusible plug on the boiler melting at a temperature below the maximum permitted temperature.
As early as 1821, it is proposed to make them mandatory also on pressure cookers of the "Papin's pot" type (Annals of the National and Foreign Industry, or Technological Mercury, 1821, p14).
A little after, the decree of October 28, 1823 imposed in France the use of two fusible plugs of different sizes on high pressure boilers (more than 2 kg/cm²), one at 10°C, the other at 20°C in below the maximum limit of the boiler. In 1828, the fusible alloy washers melting temperature, already used since several years on the safety valves of the steam locomotives, must melt at 20°C higher than that of the stamp of the boiler. The 100°C alloy is then given as composed of 8 parts of Bismuth, 5 parts of lead and 3 parts of tin. (Steam Engineers' Manual, by Janvier, 1828). In 1830, the bulletin of the laws further enacts "It will be further adapted to the upper part of each boiler, and near one of the safety valves, a metal washer fusing at the temperature of 127°C "
Different tables were established for the realization of fusible alloys for boilers. This elaboration of fusible alloys at various temperatures did not take in account the notion of eutectics, and was fatal to this application on boilers: the most fusible part of these alloys (the eutectic) gradually melting and disappearing and leaving in

	PLOMB.	ÉTAIN.	BISMUTH.	DEGRÉS de fusion.
ALLIAGES. . . .	1 partie.	3 parties.	5 parties.	Fond à 100°
	1	4	5	120
		1	1	152
		2	1	170
	2	3		168
		8	1	200
L'étain seul fond à.				228
Le bismuth				245
Le plomb				320
Le zinc.				333

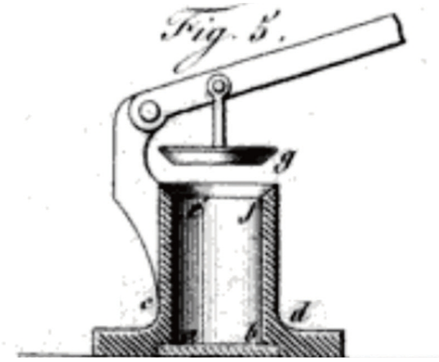
Fusible alloy composition used in steam machines (1828, Traité des machines à vapeur et de leur application à la navigation, Thomas Tredgold)

Bismuth	Lead	Tin	"Vapour pressure in Atmosphère"	Corresponding temperatures
Parts	Parts	Parts	Atmospheres	Degrees (°C)
8	6,44	3	1	100
8	8	3.80	1 1/2	112.2
8	8	7,5	2	122
8	9,69	8	2 1/2	129
8	12,64	8	3	135
8	13,30	8	3 1/2	140,7
8	15	8	4 1/2	145,2
8	16	9	5	150
8	16	19	5 1/2	154
8	25,15	24	6	158
8	27,33	24	6 1/2	164
8	28,66	24	7	168
8	29,41	24	7 1/2	170
8	35,24	24	8	173

Fusible alloy for steam machines (1875 Grand dictionnaire universel, volume 15, Larousse)

the washer the surplus of metals melting at a significantly higher temperature. The mandatory use of these fusible alloys washers and plugs for the safety of steam boilers. was abandoned in the government ordinances dated 22 and 23 of May 1843. However, in the middle of the 19th century, Darcet's low-temperature fusible alloys were widely used in industry, including metal molds for electroplating, which after use only left the outer layer of copper, thus realizing hollow objects, also allowed easier bending of tubes filled with these alloys, but also a machine named of "internal combustion" supposed to replace the steam engines to pump the water, invented in 1839 by Antoine Galy-Cazalat (often taken under the name of Galli by his laudators), professor of physics at the Royal College of Versailles, in which the fusible alloy, heated, served as a movable liquid plug and whose displacement in a spiral produced a movement.

1847 Fusible plugs on boilers of steam locomotives. Cap "e" melts and releases steam (US patent # N°5022, Alfred Stillman)



1832 Locomotive fuse plug (b), combined with a shut-off valve from Mr. Edward Hall (Bulletin de la Société d'Encouragement pour l'Industrie Nationale)

The 72°C limit: Cadmium

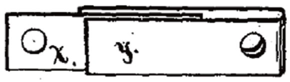
In 1817 Friedrich Stromeyer was the first to produce cadmium. But it was not until more than 30 years ago that lead, tin, bismuth and cadmium quaternary alloys appeared. The addition of cadmium reduced the melting temperature from 20 to 25°C, and went down to 72°C.

The arrival of the fire detection systems between 1860 and 1890 (alarm or sprinklers) led to the development of all current fire detection fusible links.

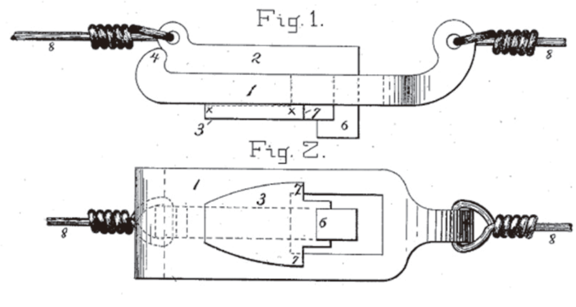
The alloy invented and patented in the USA in 1860 by the American dentist Barnabas Wood, who was later named in his honor "Wood Alloy", was first used in dentistry. It was then the first metal used for automatic sprinklers. It contains 50% bismuth, 27.6% lead, 13.4% tin and 10% cadmium. His discovery was widely commented on in Europe. ("On a New Highly Fusible Alloy," Appl. Chem. Rep., 1860, 2, 313-314 and Wood's Leichtflüssiges Metall, "Dingler's Polytech, J., 1860, 158, 271-272.). It melted at 70-72°C (158-160°F) and was then adopted as the operating temperature for sprinkler plugs in the United States and most other countries. This alloy was long time given to the USA as a 155°F alloy (68°C).

In the same year, the Berlin chemist Friedrich Julius Alexander Lipowitz, referring to the discovery of Wood, invented a close alloy: with 50% bismuth, 27% lead,

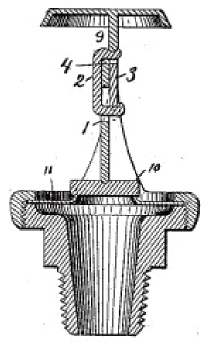
13% tin, 10% cadmium, very ductile, melting between 70-74°C. The melting point of the Lipowitz alloy, which it says is at 60°C, is only 70°C, but the confusion may be due to the fact that it also tried to introduce mercury into this alloy, which lowered its melting point to 60°C. (Polytechnisches Journal, 158, 376, 1860).
A few years later, Frederick Guthrie, in the articles he wrote in the Philosophical Magazine between 1875 and 1884 on eutectic alloys, described among others the alloy at 47.4% of bismuth, 19.4% of lead, 20% tin and 13.2% cadmium. He created in 1875, on a Greek root, the term "eutectic". (N.B.: The compositions and melting temperatures of these various alloys are clearly described in the "Encyclopedie Chimique" of Fremy, published in 1888, and may vary according to the sources, the names of the inventors being often associated with several alloy compositions).
The first fusible links appeared around 1882, and were used to command the opening of valves sending water into the fire pipes. Very quickly, the creep under permanent stress and temperature of the fusible alloys showed the possible load limits, and as early as1883 appeared the de-multiplied mechanisms.
Around 1880, the development of electrical appliances and electrical distribution networks brought out a new family of devices using fusible alloys: the fire detection electric switch, in which the melting of the alloy closed an electric circuit of alarm, either powered by batteries is powered by the network.
It was not until 1912 that the melting temperature of the eutectic alloy made of lead cadmium, tin, bismuth was confirmed at 70°C as being as low as possible with these components, but the habit was taken of naming it alloy to 72°C. (Parravano and Sirovich, Quaternary Alloys of Lead, Cadmium, Bismuth and Tin, Gazz. Chim. Ital., 42, I, p. 630; 1912)



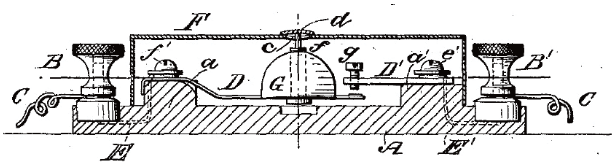
1882 Simple Fusible link used on a cable, invented by Frederick Grinnel (US patent #269.199)



1890 De-multiplied fusible link assembled on a cable (Frederick Grinnel's patent N°432403)



1890: Sprinkler head using parts welded together with a Wood's fusible alloy and aleveraging effort mechanism (Frederick Grinnel's patent N°432403)



1884 Fire alarm closing an electrical contact using fusible alloy washer (d)(US Pat. Ross No. 298121)

The 47°C limit: Indium

It was discovered by spectroscopy, in 1863, in a Freiberg blende, by Reich and Richter, who characterized it by an indigo blue line, hence the name of indium they gave it. It is related to zinc and cadmium and is extracted from their minerals. In many fusible alloys, an amount of Indium of 10 to 20% significantly lowers the melting point.
The beginning of its production in 1867 thus made it possible to further reduce the melting points: eutectic alloy of Simon Quellen Field (called Field alloy), comprising 32.5% of bismuth, 51% of indium, and 16.5%, of tin melting at 62°C (144°F)
Indium also allows to made alloys melting at a true value 155°F (68°C), still widely used in England and its former empire.
The lower limit of possible melting points with these quinquenary indium-based

alloys was reached in 1935, when the American scientist Sidney J. French, described a eutectic alloy melting at 47°C composed of 8.3% tin, 44.7% Bismuth, 22.6% lead, 5.3% Cadmium, 19.1% Indium (A New Low-Melting Alloy, Ind. Eng Chem., 1935, 27, 1464-1465, Civil Engineering, August 8, 1936)

Liquid alloys at room temperature: Gallium
In 1875 the French chemist Paul-Emile Lecoq de Boisbaudran discovered Gallium. This metal, liquid at 30°C and boiling at 2200°C, will be added to tin and indium alloys to produce alloys whose melting point can be well below 20°C. Pure gallium or alloys containing it were not used in the fusible links, but as early as 1920 to replace mercury in high temperature thermometers, and in some thermostats. Its very high price allows its use only in laboratory applications.

The appearance of the notion of eutectic (1875-1898)
The characterization of the differences between eutectic and non-eutectic alloys only appeared in the last years of the19th century, with the work of Georges Charpy. It was then realized that in the cooling of a molten non-eutectic alloy, the metals with the highest solidification temperature first began to cool and harden, leaving the liquid in the middle of the crucible an alloy whose composition eventually reached its freezing temperature. The composition of this alloy in the center was then that of the eutectic. And it was definitely lower than that of the constituent metals. The mechanisms involved in the pasty areas of non-eutectic alloys, which had caused the disappearance of fusible alloy washers in the safety systems of steam engines, were then better understood: after a while, the composition of the alloy of the washers or plugs changed: the most fusible part (the eutectic part of the alloy) was starting to melt, and the remaining metals in the washer or in the plug were melting well beyond the primitive degree. (Bismuth, tin, lead by A. Bouchonnet, 1920)
Since the fuse washer disappeared from the normative obligations of the railway boilers at the middle of the 19th century, manufacturers of industrial boilers, using only eutectic alloys, mounted them at least until 1925 (Catalog of the industrial society of Creil of 1925). Fusible alloys were still used for a long time on boiler alarm systems, and kitchen pressure cooker used eutectic alloy plugs until 1929, when they were replaced by valves (Catalog of Ateliers de Boulogne, 1929). Fusible alloys continued to be used in the safety devices, valves and thermostats of water heaters and boilers until the 1980s. (1934 Catalog of Chaffoteaux et Maury Réunis Tank)
But alloys at 70°C/72°C, whose composition was very close to the eutectic, which had only a pasty zone of 1 or 2°C are still widely used, especially in fire detection systems.

The arrival of standards concerning fire protection systems.
Many scientific publications were issued on fusible alloys. The oldest issue by a standards body seems to be "The Use of Bismuth in Fuse Alloys", Bureau of Standards » Circular No.388, 1930
In November 1968 was published in the USA the first standard (UL-33) relating to thermal links for fire protection systems "Fuse Links for Fire-Protection Service". In France, it was not until December 1990 that the standard NF S 61-937 was published where fusible links are described.
In 2005, for the first time, the ASTM B774 (Standard Specification for Low Melting Point Alloys) standard, updated in 2014, was published, which attempts to standardize fusible alloys, but gives very wide tolerances for their composition.
The binary alloys of lead and tin, in welding applications, were standardized in 1990 by the EN ISO 9453 standard.

Polemics on the measurement of liquidus and solidus temperature of eutectic and non-eutectic alloys.
This temperature measurement, complicated by the appearance of a pasty zone when

the compositions of the alloys are not exactly those of the eutectics, has been the subject of numerous scientific publications since 1701, and often gave very different results. The purity of the metals used, the temperature measuring devices and their accuracy, the location of the measuring point, the phenomena of super-fusing and recrystallization, the variation of the mechanical strength of the alloys over time, the various measuring devices of the viscosity of the alloys, the thermal differences between the center and the edges of the crucibles, the annealing and heat treatments, etc. have all participated in the melting point differences given by scientists, including even nowadays.

The arrival of Rohs environmental constraints

In 2002, the RoHS (Restriction of Hazardous Substances) European directive was published to limit the use of ten dangerous substances, including lead and cadmium, two main components of low-temperature fusible alloys. The production of low-temperature fusible alloys in accordance with this standard made it necessary to replace these two components with indium, without, however, allowing the production of entirely equivalent products. Low temperature Rohs alloys are significantly more expensive, and their mechanical strength is on average halved compared to previous ones.