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"The Accelerated Life Test of Rubber Goods"

A Review of Over 100 Years of Heat Aging According to W.C. Geer with Reference to Today's Testing Practice

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1. A Brief Historical Outline of the Early Research of Oxidation and Aging Mechanisms in Rubber

The aging of elastomers involves a great number of processes in which vulcanized rubber is chemically and physically degraded or modified. It can be triggered, accelerated or slowed down by various factors. For the practitioner and user of elastomer products, a realistic and time-shortened simulation of these processes is extremely important.

Rubber was used long before the discovery of vulcanization by Charles GOODYEAR. In 1839, GOODYEAR found more or less by chance that Sulphur and temperature reduced the stickiness of rubber and that it remained permanently elastic.
In the 1840s, the vulcanization process was continuously developed. This opened up more and more fields of application for cross-linked rubber. However, this new organic material posed many challenges for users, particularly the cracking and brittleness of the products when it was exposed to ambient air and sunlight for long periods of time.

It is difficult to find out exactly who was the first to use the term oxidation in relation to the aging of rubber. In the earliest publications on this subject in the middle of the 19th century, a distinction was often made between rubber and Gutta-percha. The latter is the latex of the Gutta-percha tree, which occurs mainly in Malaysia. Chemically, Gutta-percha (trans-1, 4-isoprene) differs from rubber (cis-1, 4-isoprene) in the configuration of the monomer. In addition, Gutta-percha contains more resin and is less elastic than rubber.
WHITBY[1], which provides a great deal of information on the origins of test methods, refers to a first mention of oxidation in a source dating from 1850[2], which, however, could not be confirmed when this quotation was verified. However, in 1851 the "Chemisch-Pharmaceutischen Centralblatt" already described typical aging symptoms of rubber or Gutta-percha. ADRIANI here quotes a report by E. WENKEBACH[3] on "the durability of rubber and Gutta Percha as a coating of telegraphic wires (...)".
Also, a coating of non-vulcanized [sic!] rubber or Gutta-percha will only withstand temperature and weather changes for a short time. On the telegraph wire attached along the Dutch railway, which has been in use for three years, the rubber coating has already completely disappeared in some places. With the Gutta-percha it is even worse; already when installing the wire covered with it, the workers complain about the change it suffers from the heat. Vulcanized rubber is to be preferred to Gutta-percha because it offers better resistance to external influences".[4] However, it was already known at that time that Gutta-percha did not show such signs of aging in seawater as in the ambient air.

Around the year 1860, the term oxidation is already found in several literature references:[5]

[1] WHITBY, G. Stafford: Plantation Rubber and the Testing of Rubber, Longmans, Green and Co., London, 1920, S.95
[2] LIEBIG, Justus und KOPP, Hermann (Hrsg.): Jahresbericht über die Fortschritte der reinen, pharmaceutischen und technischen Chemie, Physik, Mineralogie und Geologie, Giessen, 1851, S.519-521 (online verfügbar auf Hathitrust: http://hdl.handle.net/2027/nyp.33433116658463?urlappend=%3Bseq=543) (=Kurze Abhandlung über Arius ADRIANIS Werk: Verhandeling over de Gutta Percha en Caoutchouc en derzelver Verhouding tot onderscheidene Agentia,Verl. Kemink en zoon, Utrecht, 1850 und dessen Auszüge im Chem.-Pharmaceut. Centralblatt,, Leipzig, No.2, S.17ff.
[3] Translated from WENKENBACH, E. in: Notulen der vergadering van het Koninklijk Instituut van Ingenieurs, 12.Februar 1850
[4] Translated from Pharmaceutisches Centralblatt, redigiert von W. KNOP, Leipzig, 8.Januar 1851, No.2, S.23f. (Permalink: Payen 1852http://www.mdz-nbn-resolving.de/urn/resolver.pl?urn=urn:nbn:de:bvb:12-bsb10072183-7 digitale Zählung: S.29f.)
[5] The following references do not claim full coverage of the subject matter. The 1840s and 50s are full of fundamental investigations into the nature of rubber and gutta-percha, so that we can only quote examples here. A complete review of the publications of that time would be a study in itself.

- 1854/1855 Investigations by E.H. von BAUMHAUER[6] published in 1859: He tried, among other things, to obtain pure Gutta-percha in extensive chemical experiments at that time, but according to his information it is highly variable. "The cause of this is its strong oxidizability, which also makes it difficult to obtain a substance with a constant composition."[7] With his investigations he wanted to prove "that an oxygen-free substance with the probable formula C_{20} H_{16} is present in the Gutta-percha and that there are several oxidation stages of this substance, of which [his] investigations have shown determination of two, $C_{20}H_{16}O$ and C_{20} $H_{16}O_2$". BAUMHAUER continues to write: "However, I believe that in the liquid flowing out of the tree only the substance C_{20} H_{16} (...) occurs and that the other C_{20} $H_{16}O$ and C_{20} $H_{16}O_2$, and probably a whole series of such oxidation stages are caused by the influence of the air (...) This strong oxidizability of the Gutta-percha is the cause of the change which the things made of Gutta-percha suffer.
- Everyone knows that if Gutta-percha products are not covered with a good varnish, which art is better understood in England than on the Continent, they become brittle over time."[8]
- In 1859, the "Annual Report on the Progress of Chemistry" summarizes studies of recent years on Gutta-percha: Interesting here are the findings of A.C. OUDEMANS, who investigated East Indian Gutta-percha and stated: "When heated with nitric acid, it produced formic acid and a lot of hydrocyanic acid; when powdered, it absorbs oxygen, and it is difficult to store it in an unchanged form; its composition resulted from the corresponding formula C_5H_4 or $C_{20}H_{16}$".[9]

  In the summary of BAUMHAUER's publication quoted above, it is surprising that the negative influence of ozone was already known in 1860. It says: "Ozonized oxygen strongly corrodes the Gutta"[10], which is a remarkable observation only about 20 years after the first description of ozone by Christian Friedrich SCHÖNBEIN in 1839.

  The numerous new publications in the "Annual Reports on the Progress of Chemistry" of 1860 reflect the great interest in research into this new substance, rubber and Gutta-percha:

  A research project by C.G. WILLIAMS investigated the main products of the "dry distillation" (pyrolysis) of rubber and Gutta-percha. He "regarded the effect of heat on Caoutchouc as the breaking up of the latter into substances in simple polymeric relationships to the original hydrocarbon, and primarily relied on the similarity of the composition of pure Caoutchouc with that of isoprene and caoutchine".[11]

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[6] BAUMHAUER, E.H. von: Ueber die Elementarzusammensetzung der Gutta-Percha in: ERDMANN, O.L. und WERTER, G. (Hrsg.): Journal für praktische Chemie, Verlag von Johann Ambrosius Barth, Leipzig, 78. Bd., 1859, S. 277-287 (Permalink zu diesem Artikel: http://hdl.handle.net/2027/hvd.hxgq6g?urlappend=%3Bseq=291)
[7] Translated from Ebd., S. 281 (Permalink zu dieser Seite: http://hdl.handle.net/2027/hvd.hxgq6g?urlappend=%3Bseq=295)
[8] Ebd., S. 285 (Permalink zu dieser Seite: http://hdl.handle.net/2027/hvd.hxgq6g?urlappend=%3Bseq=299)
[9] Translated from KOPP, H und WILL, H. (Hrsg.): Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften für 1859, J. Ricker'sche Buchhandlung, Giessen, 1860, S. 518 (Permalink zu dieser Seite: http://hdl.handle.net/2027/mdp.39015065229786?urlappend=%3Bseq=542)
[10] Translated form Ebd., S. 519
(Permalink zu dieser Seite: http://hdl.handle.net/2027/mdp.39015065229786?urlappend=%3Bseq=543)
[11] Translated from Ebd., S. 495
(Permalink zu dieser Seite: http://hdl.handle.net/2027/nyp.33433116658562?urlappend=%3Bseq=523)

Also discussed in this annual report were A. ADRIANI's findings that "in very pure Gutta-percha he found 87.91 pC. %] C and 11.94 H, and in those which had become brittle, one up to 20 pC. (Caoutchouc, too, is subject to such a change, although more slowly...)". [12]

- In a report for the "Director-General of Telegraphs in India" HOFMANN investigates the brittleness of Gutta-percha, which lost its cohesion within a short time during the construction of the "East Indian Telegraphs" and became absolutely useless and caused high downtime costs. At the end of his essay, published in 1861, he writes: "That the changes of Gutta-percha are due to the absorption of oxygen, is countenanced by the experience of this substance having been kept for years under water without undergoing any alteration".[13]
- In 1865 Spiller reports on his investigations of aged "India Rubber". He compared the evaporation residue after extraction of new so called "patented waterproof felt" with the one, stored for six years and compared the results with those of A.W. Hofmann for "Gutta Percha", mentioned above. The resin obtained from the aged material is also referred to in literature as "Spiller's resin". He found similar C-, H- and O-parts as HOFMANN and Spiller wrote: "For the reason adduced by Dr. Hofmann in the case of the altered Gutta-percha examined by him, I abstain from constructing a formula, and merely regard this substance as an oxidation product formed directly from caoutchouc by the absorption of atmospheric oxygen, in much the same manner as resins are formed from essential oils and other hydrocabons.". [14]

In the "Journal of the Society of the Chemical Industry", W. THOMSON 1885[15] publishes detailed and practice-oriented studies on the aging of rubber threads. Research is now moving more and more from a once purely chemical interest in this material to application practice, which is to be improved and facilitated with chemical knowledge.
For example, the problem of over and undercure and its effects on aging is already addressed, and simple measuring methods for checking the degree of cure are suggested (measurement of the elongation of a rubber thread with a pre-defined weight). The influence of the solar radiation and increasing temperature and elongation on aging is discussed, as is the fact that aging takes place from the outside to the inside. In microscopic investigations it could be determined that the rubber at that time still had a kind of cell structure (enclosed air bubbles). The aging on the walls of the bubbles was stronger than in the solid material between the bubbles. Another remarkable finding is that "ozonized air has little effect on unstretched or relaxed rubber, but reacts very quickly to rubber in the stressed or stretched state".[16]
In the following decades, this versatile material was further intensively researched. The numerous publications by Carl Dietrich HARRIES are significant in the field of the effect of

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[12] Translated from Ebd., S. 496
(Permalink zu dieser Seite: http://hdl.handle.net/2027/nyp.33433116658562?urlappend=%3Bseq=524)
[13] HOFMANN, A.W.: Remarks on the Changes of Gutta Percha under Tropical Influences in: The quartely journal of the Chemical Society of London, Vol. 13, 1861, S.90 (Permalink zu dieser Seite: http://hdl.handle.net/2027/uc1.31822004301057?urlappend=%3Bseq=98)
[14] SPILLER, John: On the Oxidation of India Rubber in: WATTS, Henry (Hrsg.): The Journal of the Chemical Society of London, Vol. 18, 1865, S.44 (Permalink zu dieser Webseite: http://hdl.handle.net/2027/mdp.39015077817644?urlappend=%3Bseq=62)
[15] THOMSON, William: India Rubber and its Decay in: The Journal of the Society of Chemical Industry, Dec.29, 1885, S. 710-719
[16] Ebd., S. 716

ozone, which also describes a special type of oxidative aging of rubber. He has dealt intensively with this well-known topic.[17]
After 1906, according to GEER[18], most investigations on aging dealt with the theoretical background of oxidation, the analysis of oxidation products and the investigation of aging to determine the optimum degree of cross-linking.
In the following, only a few examples will be presented: [19]
In 1918, PEACHEY and LEON[20] published results on the influence of moist oxygen on raw and cross-linked rubber. Rubber oxidized much more slowly than raw rubber, but both absorbed about the same amount of oxygen.
BING[21] found sulphuric acid in vulcanized rubber and investigated the strong degradation and aging of rubber by copper chloride. However, the degradation of rubber by copper was first described in 1865 by MILLER[22], who investigated the rubber insulation of copper cables.
In the years following the public presentation of heat aging, the processes involved were examined in ever greater depth and detail, both from a purely chemical point of view and with reference to practical application issues. For further information, please refer to the relevant technical literature.

2. First Accelerated Aging Tests

According to W.C. GEER[23], C.O. WEBER developed the first practical accelerated aging test around 1900. WEBER calls his test "sun cracking test"[24] because at that time the belief prevailed that oxidation was caused and accelerated mainly by sunlight. Since storage in the air depends very much on the respective weather and is therefore not a practical option, it was not pursued any further. Storage in ozone was also examined, but back then it was not easy to ensure a constant ozone concentration. WEBER proposes instead a mixture of 20 gr. acetone with 60 ccm of a 20% hydrogen peroxide solution.[25] After a 14-day rest period, storage can begin. Equally sized test strips of the material to be tested and the reference material are weighed and then placed in the solution described above for at least two days. After removal, the specimens are cleaned with acetone and dried at 100°C. The increase in weight was then

[17] HARRIES, Carl Dietrich: Ueber den Abbau des Parakautschuks vermittelst Ozon in: Berichte der deutschen chemischen Gesellschaft, Commissionsverlag von R. Friedländer & Sohn, Berlin, 37. Jg., Juni **1904**, S. 2708-2711
[18] GEER, William C. und EVANS, Walter, W.: Ten Years' Experience with Aging Tests in: India Rubber World,1September 1921, S. 888 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050937)
[19] *Die folgenden Forschungsergebnisse wurden der Aufstellung von GEER und EVANS entnommen:* GEER, William C. und EVANS, Walter, W.: Ten Years' Experience with Aging Tests in: India Rubber World,1September 1921, S. 888f. (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050937)
[20] PEACHEY, S.J. und LEON, M.: The Oxidation of Rubber (?) in: Journal of the Society of Chemical Industry, Issue 4, Vol. 37, 28Feb 1918, S. 55T-60T
[21] BING, Kai: Ueber freiwillige Veränderungen von vulkanisiertem Kautschuk in: Kolloid-Zeitschrift, Vol. 4, Issue 5, 1909, S.232ff.
[22] MILLER, William Allen: On the Decay of Gutta-percha and Caoutchouc in: Journal of the Chemical Society, Vol. 18, 1865, S. 273-284
(Weblink zu diesem Artikel: http://hdl.handle.net/2027/mdp.39015077817644?urlappend=%3Bseq=289)
[23] GEER, William C. und EVANS, Walter, W.: Ten Years' Experience with Aging Tests in: India Rubber World,1September 1921, S. 887. (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050936)
[24] WEBER, Carl Otto: The Chemistry of India Rubber including the Outlines of a Theory on Vulcanisation, Charles Griffin and Co., London, 1902, S. 229f.
[25] Acetonperoxid nach C.O. WEBER im trockenen Zustand hochexplosiv ist, sollte es nicht isoliert werden.

taken as a measure of the oxygen absorbed and the resistance to sun cracking. WEBER found a relatively good correlation with the results from real sun exposure over longer periods of time.

In 1906, DITMAR published in the “Gummi-Zeitung” a laboratory method for testing the durability of rubber. "It was based on the assumption that the durability of rubber and of rubber goods varied inversely to the ease with which they were oxidized by atmospheric oxygen […] The sample to be examined was rolled into a thin sheet and dried to constant weight in vacuum over calcium chloride or in a drying oven at 100 degrees C. Four-tenth to eight-tenths-gram of the dried sample was then sealed in a thick-walled’ tube from which the air had been displaced by oxygen and heated for 5 to 20 hours at 100 degrees C. The tube was then allowed to cool, the rubber removed, weighed rapidly and the increase in weight taken as an inverse measure of the durability of the sample. The increase in weight shown by a sample of good rubber in five hours amounted from 2 to 4 per cent.” [26]

The tensile strength was already an important criterion for the quality of rubber products from early on.[27] It was found that the results of the tensile test (including elongation at break and stress values) were strongly influenced by aging. For this reason, practical orientated aging research always tried to age test specimens, which can then be examined and evaluated in the subsequent tensile test. In the 1920s and 30s there was a tendency towards a continuous shortening of the test times, so that sometimes some unrealistic boundary conditions occurred (such as storage under gas pressure). These rapid methods, which will be briefly described in the following chapter, however, could not be established permanently in day-to-day testing.

3. ACS-Symposium 1916

3.1 53rd Annual Meeting der ACS 1916 in New York City

At the end of September 1916, the 53rd Annual Meeting of the ACS (American Chemical Society, which is today’s world's largest scientific society with 158,000 members) was held in New York City. More than 2000 members were registered and the lectures were held over five days. At the same time, the second national exhibition of the chemical industry was held with 200 participating companies. The Rubber Section met in the Rumford Hall of the Chemists' Club and was chaired by Dr. Lothar E. Weber.[28]
About 20 chemists took part in a symposium entitled "The Accelerated Life Test of Rubber Goods".

[26] GEER, William C. und EVANS, Walter, W.: Ten Years‘ Experience with Aging Tests in: India Rubber World,1September 1921, P. 887f. (Weblink to this page: http://biodiversitylibrary.org/page/7050936)
[27] Vgl. MAASEN, G.C.: Introduction in: Symposium on Aging of Rubbers, Chicago Spring Meeting ASTM Special Technical Publication No. 89, March 1949 S. 1
[28] The Chemical Convention and Exposition in: The India Rubber World, 1October 1916, S. 6 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7113229 , abgerufen am 05.09.2016)

3.2 Presentation of the New Aging Test in the "Rubber Section" of the ACS by Dr. W.C. GEER and Interesting Facts from the Following Discussion

After introductory words by Dr. L. Weber, “Dr. Geer then spoke briefly regarding his methods, as follows: The first work done in the laboratories of The B. F. Goodrich Co. on accelerated age tests was in the fall of 1907, at which time a suggestion came to us from Dr. Van der Linde, of the Gutta Percha & Rubber Co. [29], at Toronto, who used a very fast aging test. He performed it upon three small pieces of rubber. The samples to be tested were put in an air bath and heated at about 140 °C for a period of 1, 2 and 3 hours, taken out and examined for cracking, hardening or to ascertain whether it was becoming soft. This method was not parallel with actual aging in any particular and we came to the following: Into an oven [**Fig. 2**], heated air was blown at a temperature of 160 degrees F., the chief care being to add hot fresh air during the desired time. A number of samples 3/32 of an inch in thickness were previously cut and put into this air bath. The air then started circulating and the test was continued for a period of two weeks, taking out three samples each day. These were allowed to stand for 24 hours until they reached a state of equilibrium. After which they were tested for tensile strength and elongation at break. The data was plotted in curve form and gave us a time decay curve of the compound. It is worthwhile to emphasize that we consider this a purely practical, and not an ultimate test. It was always run in comparison with standard compound; that is at least two sets of samples were tested at the same time.”[30]

Already in 1916 GEER described: “We have run many thousands of these curves […]. We now have the results of ordinary aging tests plotted in months, in comparison with the accelerated aging tests plotted in days for the same compound […] [graphic representation in **Fig. 4**]. Dr. Geer stated that his tests were carried out under air conditions and in the dark. His samples were put in a drawer separated by a sheet of cardboard, and the temperatures given were varying to a certain extent, although the temperature of the room did not ordinarily exceed 95 degrees in summer and never became very cold in winter as there was continuous heat.”[31]

Natural aging could also be carried out in hanging cabinets, as the following **Fig. 1** from the US "Bureau of Standards" proves.

[29] Katalog der Gutta Percha and Rubber Manufacturing Company, Toronto, Kanada aus dem Jahr 1910: https://archive.org/details/mechanicalrubber00guttuoft (Webseite abgerufen am: 06.09.2016)

[30] Dr. W.C. Geers in: The India Rubber World: The Accelerated Life Test of Rubber Goods, IRW, 55, 1December 1916, S. 127 Weblink zu dieser Seite (abgerufen am 02.09.2016) http://biodiversitylibrary.org/page/7113354

[31] *ibid*

Fig. 1: Natural aging in hanging cabinets in the "Bureau of Standards", around 1927[32] (Reproduced with kind permission of the National Institute of Standards and Technology, U.S. Department of Commerce.)

Special attention was also paid to the optimum degree of cross-linking. Under-cured test specimens did not pass the test.

This image can be viewed under the following link: http://biodiversitylibrary.org/page/7050937 (see also Fig.1)

Fig. 2: "The Black Art of Rubber Testing": Heat aging according to GEER, around 1920, presumably in the laboratories of B.F. Goodrich, Akron, Ohio [33]

[32] TENER, R.F.; SMITH, W.H.; HOLT, W.L.: Aging of Soft Rubber Goods in: Technologic Papers of the Bureau of Standards, No. 342 (Part of Vol. 21), Department of Commerce, Bureau of Standards, June6 1927, Bildtafel 2 nach S. 358 (Weblink zu dieser Veröffentlichung (abgerufen am 03.10.2016): http://nvlpubs.nist.gov/nistpubs/nbstechnologic/nbstechnologicpaperT342.pdf)

[33] GEER, William C. und EVANS, Walter, W.: Ten Years‘ Experience with Aging Tests in: India Rubber World,1September 1921, S. 888 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050937)

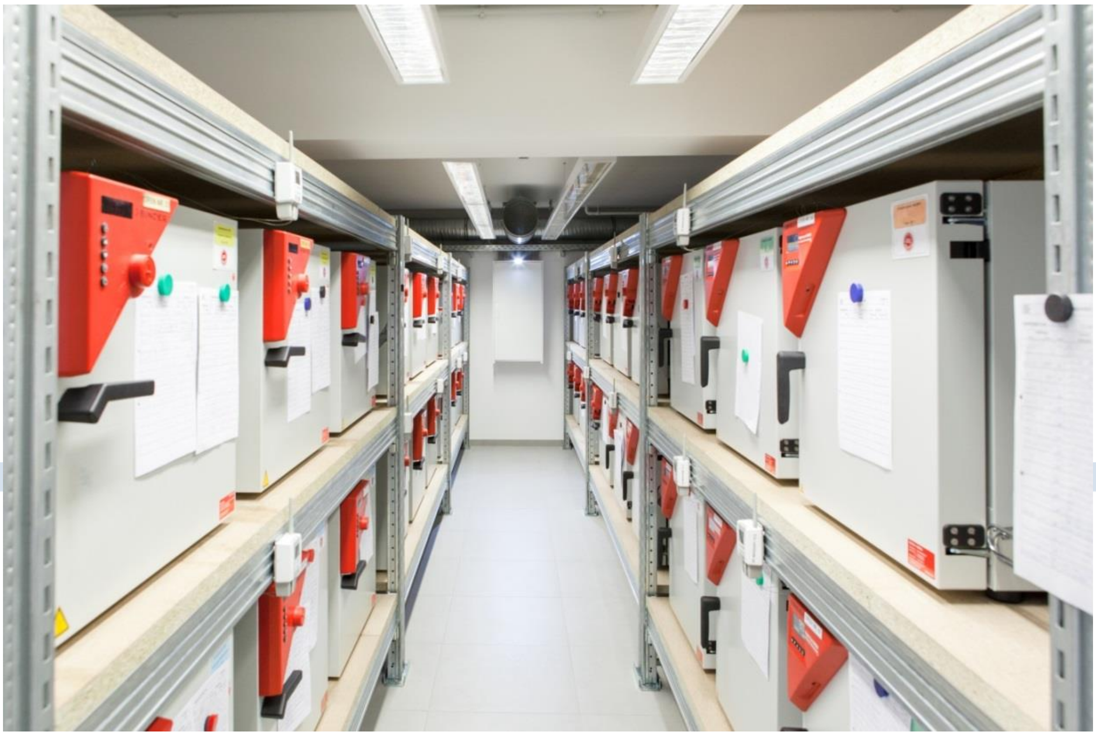

Fig. 3: Heat aging according to W.C. GEER in 2016
(Photo: O-Ring Prüflabor Richter GmbH)

The following curve (**Figure 4**) with results from the tensile test (tensile strength) is rather unusual for today's reader, as modern specifications have reduced the testing effort to the extent that a maximum of only three storage durations are carried out (e.g. 168h, 504h and 1008h). At GEER's early beginnings, 7 days of heat aging storage resulted in daily, sample removals and evaluations, as the diagram below shows. This was a kind of step aging.

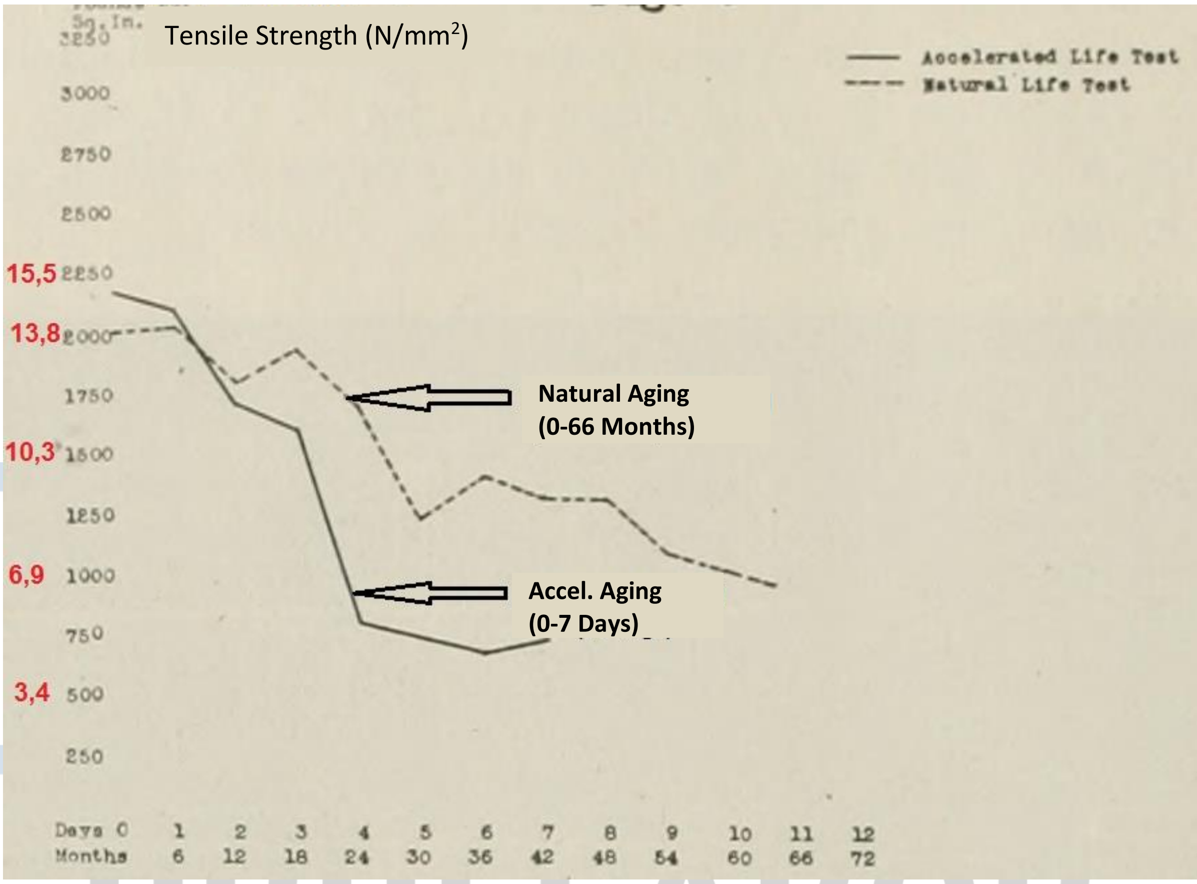

Fig. 4: Comparison of natural and accelerated aging: The X-axis shows the days for natural aging at the top and the months for accelerated artificial aging at the bottom[34] (image from the Biodiversity Heritage Library, digitized by New York Botanical Garden, LuEsther T. Mertz Library, www.biodiversitylibrary.org, edited and supplemented by O-Ring Prüflabor Richter).

The more similar these diagrams were in shape, the more it was assumed that the GEER test provided realistic results. It should be noted though, that at that time most rubber articles were only used at ambient temperatures, which is why comparison with natural aging at room temperature was so important. Today this temperature range is rather rare for technical elastomers (except for tires).

In 1916 GEER saw its aging test primarily as an instrument for the compounder in the development of compounds and advises not to use it as a specification test at the end user of the product, except for articles stored for long periods such as fire hoses. He found his test only helpful for higher quality compounds and not reliable for inferior compounds or compounds for special applications.

For him, it was a practical accelerated test for elastomers in standard applications, not for compounds in contact with light or lots of steam.

In the subsequent discussion after GEER's lecture, it became apparent in the contribution of a certain C.R. BOGGS that it was already known in 1916 how aging by exposure to light or

[34] GEER, William C. und EVANS, Walter, W.: Ten Years‘ Experience with Aging Tests in: India Rubber World,1September 1921, S. 890 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050939

acetone peroxide (see Chapter 2) causes other damage than simply heat aging. BOGGS reports a good correlation between results from natural aging and those from GEER heat-aging. According to his own accounts, he had already been using this test for several years in 1916. According to him, there would be - depending on the quality of the compound - deviations in the correlation of storage days according to the GEER method to exposure months during natural aging, but this does not affect the test itself. BOGGS even recommends to demand the GEER test as a quality feature, as this would create clarity for both the customer and the manufacturer.

Finally, Dr. WEBER reports on his own aging experiments. He stored a compound whose aging properties he knew for two weeks at 65°C together with an unknown compound. After this time, he compared the two samples and drew conclusions about the aging behavior of the unknown compound. It was important to him that the compound composition was similar to that of the compounds to be compared. He found that the damage caused by heat increased as the rubber content in the compound increased.

GEER presented his method and results in very modest words in 1916. But from today's point of view it is remarkable to see how much he did knowingly or intuitively right already at the beginning of the development of the test method, such as the regular air changes, the deposits in the dark, the choice of a not too high temperature, the use of relatively thin specimens (approx. 2.4 mm) and the avoidance of contact between the specimens.

4. The Life of Dr. William Chauncey GEER

Dr. William Chauncey GEER (**Fig. 5**) was born in Ogdensburg on the St. Lawrence River on the border to Canada in 1876. After graduating 1902 in chemistry from Cornell University in Ithaca, which, like his birthplace, is located in the state of New York (AB degree, equivalent to B.A.) he received his doctorate in 1905 from the same university. The title of his dissertation was "Contributions to the Chemistry of Indium". It was also published as a book in 1912[35]. This thesis does not yet indicate any turning to the rubber industry, but interestingly, indium is used today for special seals in cryostats, since it is known that elastomer seals fail at very low temperatures. From 1904 to 1906 he was a lecturer at Cornell University. He then worked for a year as a wood distillation expert for the U.S. Forest Service. During this time, he published a paper on the analysis of turpentine oil

Fig. 5: Dr. William Chauncey GEER (*1876-1964), photograph taken around 1916[37]

[35] GEER, W.C.: Contributions to the Chemistry of Indium, Eschenbach Printing Company, Easton, Pa., 1912 (Webseite abgerufen am 02.09.2016: https://newcatalog.library.cornell.edu/?click_to_search=true&commit=search&q=%22Geer%2C+William+Chauncey%2C+1876-%22&search_field=author_cts_search)

[37] The India Rubber World: The Accelerated Life Test of Rubber Goods, IRW, 55, 1December 1916, S. 127 Weblink

from fractional steam distillation[36], published by the Department of Agriculture's Forest Service. The Forest Service was apparently interested in the composition of turpentine oil made from yellow pine waste wood.

(Image from the Biodiversity Heritage Library, digitized by New York Botanical Garden, LuEsther T. Mertz Library, www.biodiversitylibrary.org)

Furthermore, the passing on of chemical knowledge was very important to him as a lecture he held about the way chemistry was taught in secondary schools at that time proves. [38]
In 1908 he married the two-year older Effie Work, whose eldest brother Bertram G. WORK (1868-1927) was General Director of B.F. GOODRICH from 1907 until his death in 1927.[39] William GEER had two daughters with Effie Work.
The company GOODRICH was founded in 1870 by Dr. Benjamin F. GOODRICH in Akron, Ohio. It was one of the four major tire manufacturers (Firestone, General Tire, Goodyear and B.F.Goodrich) in the Rubber Capital of the World, as Akron is sometimes called. In 1986 it merged with Uniroyal. The tire product line was sold in 1988 to Michelin, who still markets this name.[40] Until about 1900, American rubber manufacturers rarely employed chemists. It is Benjamin GOODRICH's great achievement to have recognized early on that rubber production requires not only mechanical but also chemical knowledge. For this reason, he soon hired a German chemist[41] and founded the first rubber research laboratory in the USA in 1895[42].
It is therefore understandable that GEER, as a chemist in this company, had great opportunities for development and career promotion. In the course of his working life, he held various management positions: chief chemist (1907-1916), head of development (1916-1918), second deputy director of development (1918-1920) and deputy director of research and development (1920-1925).
The beautiful mansions that GEER and his father-in-law had built show that it was still possible to earn a lot of money with elastomers at the time. William GEER obviously had a preference for English style houses. Until 1925 he lived in a building in the Free English Manorial style[43] (**Fig. 6**) and moved to Ithaca in 1929, where he built the house Far Horizons (**Fig. 7**) in the English Cottage Style.

zu dieser Seite (abgerufen am 02.09.2016) http://biodiversitylibrary.org/page/7113354

[36] GEER, William C.: The Analysis of Turpentine by Fractional Distillation with Steam, U.S. Department of Agriculture Forest Service Circular 152, 1908 (Buch online verfügbar: https://archive.org/details/analysisofturpen15geer)

[38] GEER, William C.: The Teaching of Chemistry in the Secondary Schools: A Study of Recent Practice and Results in: The School Review, April 1906, S 275ff. (Aufsatz online verfügbar: https://archive.org/details/jstor-1075658)

[39] These and other life data are taken from the following sources: “Cayuga Heights History Project”: http://cayugaheightshistory.weebly.com/630-highland-rd.html und http://cayugaheightshistory.weebly.com/624-highland-rd.html Webseiten abgerufen am 02.09.2016 und
GEER, W.C: Goodyear Rubber Award Address: Strategy in Rubber Research in: Industrial & Engineering Industry, Nov. 1951, 43. Jg., S. 2436-2440

[40] Vgl. https://de.wikipedia.org/wiki/Goodrich_Corporation (Webseite abgerufen am 02.09.2016)

[41] The Chemical Convention and Exposition in: The India Rubber World, 1October 1916, S. 8 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7113231 abgerufen am 05.09.2016)

[42] Polycorp – About us, S.2 http://www.poly-corp.com/assets/file/resource/POLY_Insert_Corporate_AboutUs_Ver2-R5.pdf S.2 (Webseite aufgerufen am 06.09.2016)

[43] The Greer-Yeager House: http://www.summitmemory.org/cdm/search/field/title/searchterm/Greer-Yeager (Vermutlich handelt es sich hier um einen Tippfehler und es müsste wohl richtig “**Geer**-Yeager-House” heißen.)

This image can be viewed under the following link: http://www.summitmemory.org/cdm/singleitem/collection/building/id/288/rec/2

Fig. 6: The "Greer Yeager" house in Akron, where the GEER family lived until 1925 (photograph taken in 1913) [44]

This image can be viewed under the following link: http://cayugaheightshistory.weebly.com/630-highland-rd.html (siehe zweites Bild in schwarz-weiß)

Fig. 7: The house "Far Horizons" in Ithaca, N.Y., completed in 1930 with twelve rooms in the English country house style, the bricks of the facade were fired in such a way that they looked like historical stones.[45]

His father-in-law B.G. WORK owned a castle-like mansion "Oak Knoll"[46] (**Fig. 8**), which was recently on sale for over 12 million US$[47] and to which a whole Facebook page is dedicated.[48]

Pictures of Oak Knoll can be found under the following link: https://www.facebook.com/media/set/?set=a.490584494311627.94941.203151249721621&type=3

Fig. 8: Oak Knoll - Villa of B.F. Goodrich Director Bertram G. Work [49]

In 1925, at less than 50 years of age, William GEER retired for health reasons, yet he continued to be very active in elastomer research in his own laboratory ("William C. Geer Laboratory"). He had built this laboratory next to his country house in the same style. There he developed "de-icing shoes" for aircraft wings (**Fig. 9**) with the support of the Guggenheim Foundation and his former employer. (US Pat. 1,998,809, dated April 23, 1935) An inflatable rubber coating made it possible to flake off the ice formed on wings.[50] The invention is still used today in smaller aircrafts.

[44] Source of photography: http://www.summitmemory.org/cdm/singleitem/collection/building/id/288/rec/2
[45] Source of photography: http://cayugaheightshistory.weebly.com/630-highland-rd.html
[46] "Oak Knoll" auf Google Earth: http://wikimapia.org/#lang=de&lat=40.882122&lon=-73.548837&z=18&m=b&v=2 (Webseite abgerufen am 02.09.2016)
[47] VILADAS, Pilar: Your Next Long Island Weekend Home - This impeccably designed home, by the architect behind John D. Rockefeller's Pocantico Hills estate, could be yours for just $12.8 million in: www.townamdcountrymag.com Aug7, 2014 (Webseite abgerufen am 02.09.2016: http://www.townandcountrymag.com/leisure/arts-and-culture/reviews/a1652/oak-knoll-mill-neck-for-sale/)
[48] "Oak Knoll" Bertam G. WORKs Landvilla auf Facebook: https://www.facebook.com/media/set/?set=a.490584494311627.94941.203151249721621&type=3 (Webseite abgerufen am 02.09.2016)
[49] Facebook-Page from „Oak Knoll" Bertram G. Work Estate (in der Rubrik „King Views of Philadelphia"): https://www.facebook.com/media/set/?set=a.490584494311627.94941.203151249721621&type=3 (Webseite abgerufen am 03.09.2016)
[50] Description of this invention in the literature of the time: https://books.google.de/books?id=u-IDAAAAMBAJ&pg=PA234&dq=Popular+Mechanics+1931+curtiss&hl=en&ei=3bTyTKD7AZPfnQeEr635Cg&sa=X&oi=book_result&ct=result&redir_esc=y#v=onepage&q&f=true
And the magazine Flying (siehe S.43): https://books.google.de/books?id=vlMkwy54cTAC&lpg=PA44&ots=jdpH1IQNgM&dq=ice+removing+overshoe&pg=PA4&redir_esc=y#v=onepage&q=ice%20removing%20overshoe&f=false

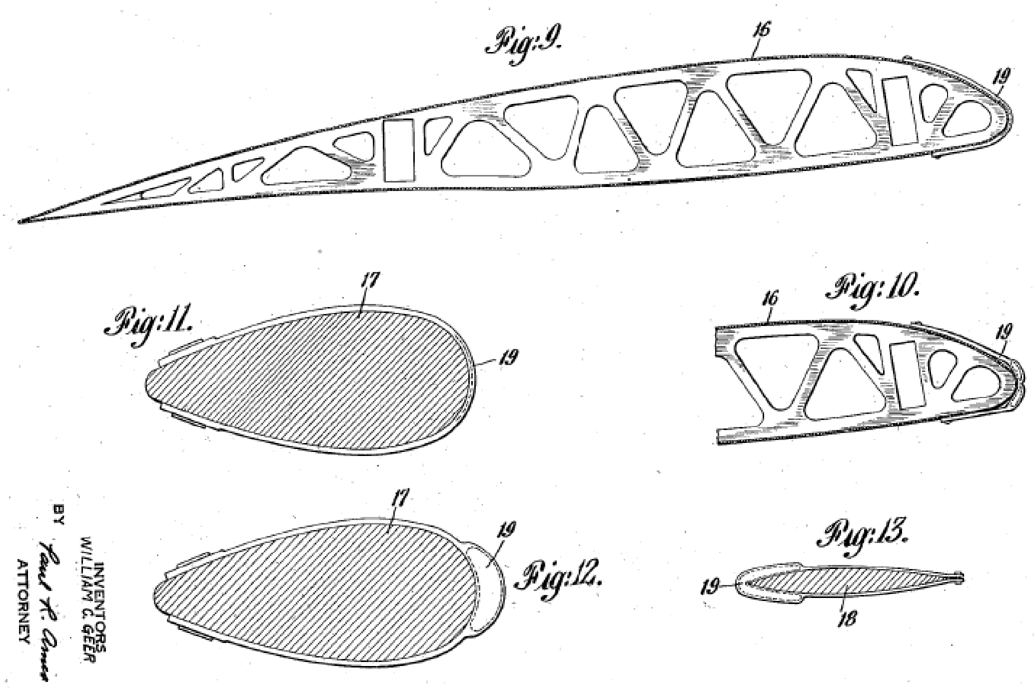

Fig. 9: Excerpt from William C. GEER's US patent 1,998,809 for de-icing aircraft wings: The inflatable "rubber overshoes" are marked with number 19.[51]
(Source: United States Patent and Trademark Office, https://www.uspto.gov/)

Almost 40 patents[52] can be found under the name William C. GEER, ranging from an improved gas mask of the 1920s (US Pat. 1,364,104), novel adhesives (US Pat. 1,744,880) to gas impermeable materials for airships (US Pat. 1,801,666).
He also became known for vulcanized golf ball coatings and Vulcalock adhesives for rubber-to-metal bonding.
He also published many scientific articles and in 1922 a book entitled "The Reign of Rubber"[53] in which he covers a wide range from raw materials over the development of the rubber industry and its important products. It seems that in rubber he had found the material that had a profound influence on his whole life and thinking. In his outlook on the future of rubber (chapter XXI in "The Reign of Rubber"), his view of the big picture and comprehensive interrelationships becomes tangible.
His life's work was honored in 1951 when he was awarded the prestigious Charles Goodyear Medal by the Rubber Division of the American Chemical Society.
William C. Geer passed away on September 9, 1964 in Ithaca, N.Y. at the age of 88. He appears to have been a well-known researcher in the USA and beyond, as an obituary appeared in the New York Times[54] on September 10, 1964.

[51] US patent 1,998,809 dated 23 April 1935, inventor William C. Geer: Means and Method for Controlling the Accumulation of Ice upon Surfaces Exposed to Ice Forming Conditions, S.3
[52] Listing of patents under the name "William C Geer" at the US Patent Office: http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO2&Sect2=HITOFF&u=%2Fnetahtml%2FPTO%2Fsearch-adv.htm&r=0&p=1&f=S&l=50&Query=IN%2FGeer-William-C&d=PALL (Webseite abgerufen am 29.11.2016)
[53] GEER, William C.: The reign of rubber, The Century company, New York, 1922 (Diese Buch ist online abrufbar: https://archive.org/details/reignofrubber00geer)
[54] Nachruf auf W.C. Geer in der New York Times vom 9. September 1964: http://www.nytimes.com/1964/09/10/william-c-geer-inventor-dies.html?_r=0 (Webseite abgerufen am 02.09.2016)

5. "Ten Years of Experience with Aging Tests"[55]

In June 1921, William C. GEER and Walter W. EVANS, Head of Development at B.F. GOODRICH, lectured at the International Rubber Conference in London on their experiences with accelerated aging tests. This was published in September 1921 in "The India Rubber World" under the title of this chapter. Meanwhile, according to B.F. Goodrich, he held many thousands of aging diagrams, some of which he presented publicly at the IRC in London. Due to the large testing effort (daily removal), this could only have been possible with well-organized procedures and a large number of furnaces, as **Fig. 10** shows.

This image can be viewed under the following link: http://biodiversitylibrary.org/page/7050938 (see also Fig.2)

Fig. 10: Frontal and plan view of a furnace system for heat aging according to GEER, most likely designed by GEER himself and his colleagues. GEER had the advantage of being able to carry out all tests at the same constant temperature so that one heat source could supply several furnaces side by side**.**[56]

After a detailed introduction on the state of research at that time, GEER and EVANS describe their test conditions in detail, which in **Tab. 1** are compared to today's test practice. It is fascinating to discover how precisely and how early decisive points were defined by GEER and colleagues:

1921: Test Conditions According to GEER and EVANS	2016: Testing Practice of an Internationally Active German Elastomer Testing Laboratory
160°F (=71°C) constant test temperature over the entire test cycle	Due to more heat-resistant compounds, the 70°C are hardly used today. However, GEER's groundbreaking innovation of testing in the upper maximum temperature range but not above that of the respective compound has been established since then.
Continuous supply of hot fresh air throughout the test cycle	Most aging tests today are carried out in accordance to ISO 188, "Method B, Type 1" in thermal ovens (forced ventilation with laminar flow).
Specimens with a uniform thickness (3/32 inch) are put into the format required later (e.g. test rod for tensile test) before the test.	The most frequently used S2 and S3A shoulder bars (according to DIN 53504) are punched out of 2mm thick test plates.

55 This chapter presents the results of the following lecture: GEER, William C. und EVANS, Walter, W.: Ten Years' Experience with Aging Tests in: India Rubber World,1September 1921, S. 887-892 (Weblink zu diesem Artikel: http://biodiversitylibrary.org/page/7050936)

56 GEER, William C. und EVANS, Walter, W.: Ten Years' Experience with Aging Tests in: India Rubber World,1September 1921, S. 889 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050938)

A hole is punched into the shoulder of the test rod. The test rods are threaded onto a wire with a small rubber disc as a spacer so that the entire surface can be flushed with hot air.	This is still done with small deviations. In the heating cabinet we use stands (see **Fig. 13**), which avoid any contact (also with rubber spacer plates) and in the narrow cell-type oven we use ceramic spacer rings (see **Fig. 12**), in order to avoid any migration of compound components.
The test lasts 2 weeks in which three specimens are removed daily.	Most tests today still run for a week or even multiple weeks. Examinations of, e.g. 10 days, are rather unusual.
Before the tensile test, the specimens should relax in a normal climate for 24 hours.	According to ISO 188, the specimens should rest at room temperature for at least 16 hours to a maximum of six days after removal from the furnace.
The manufacturer FREA recommends furnaces with an internal turbulence also called agitator.	ISO 188 distinguishes between Type 1 (= laminar flow) and Type 2 (= turbulent flow) for furnaces with forced ventilation. Nowadays, furnaces with laminar flow are used more frequently.
Testing without increased pressure (normal atmosphere)	Test methods applied temporarily with increased pressure (e.g. oxygen bomb according to BIERER-DAVIS) have not been established permanently.

Tab. 1: Comparison of important test parameters of heat aging according to GEER in 1921 and 2016

This image can be viewed under the following link:
http://biodiversitylibrary.org/page/7050937
(see also Fig.1)

Fig. 11: In the open GEER oven no. 6, a closer look reveals how shoulder bars are suspended freely from a probably removable plate with a wire and the spacers described by GEER and EVANS. Photo taken around 1920[57]

Fig. 12: The C specimens for hot-air storage in the cell-type ovens according to ASTM D865. The white ceramic rings prevent contact between the shoulder rods. Contact migration of constituents allow air contact on all sides (Photo: O-Ring Prüflabor Richter GmbH)

[57] GEER, William C. und EVANS, Walter, W.: Ten Years‘ Experience with Aging Tests in: India Rubber World,1September 1921, S. 888 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050937)

Fig. 13: Modern specimen holder in the heating cabinet, which prevents any contact between the specimens and ensures ideal contact with the furnace air. As in GEER's times, the shoulder rods are still punched in the wider shoulder area for the suspension (Photo: O-Ring Prüflabor Richter GmbH)

The picture can be viewed under the following link: https://archive.org/details/FreasElectricConstantTemperatureDryingOvens (see p.9 or p.10 according to the count of the PDF)	The picture can be viewed under the following link: https://archive.org/details/FreasElectricConstantTemperatureDryingOvens (see p.16 or p.17 according to the count of the PDF)
Fig. 14: Electric drying oven with constant temperature around 1920 (FREAS brand, Type R, No. 108) - FREAS was recommended by GEER [58]	**Fig. 15:** Electric drying oven with constant temperature and forced air circulation, here mainly for drying moist objects, around 1920 (brand FREAS, type FA, No. 101) - FREA was recommended by GEER [59]

Below are some examples that GEER and EVANS presented to the public in 1921:
In **Fig. 16** an old compound type for rubber threads was investigated. Only results from heat aging over a seven-day period are presented. The rapid degradation is significant here. Already after four days at 70°C the tensile strength drops to less than 10% of the initial value.

[58] THERMO ELECTRIC INSTRUMENT Co. (Hrsg.): Freas: electric constant temperature drying ovens (Firmenprospekt), ca. 1920, S. 9
(Broschüre digital abrufbar: https://archive.org/details/FreasElectricConstantTemperatureDryingOvens)
[59] Ebd., S.16

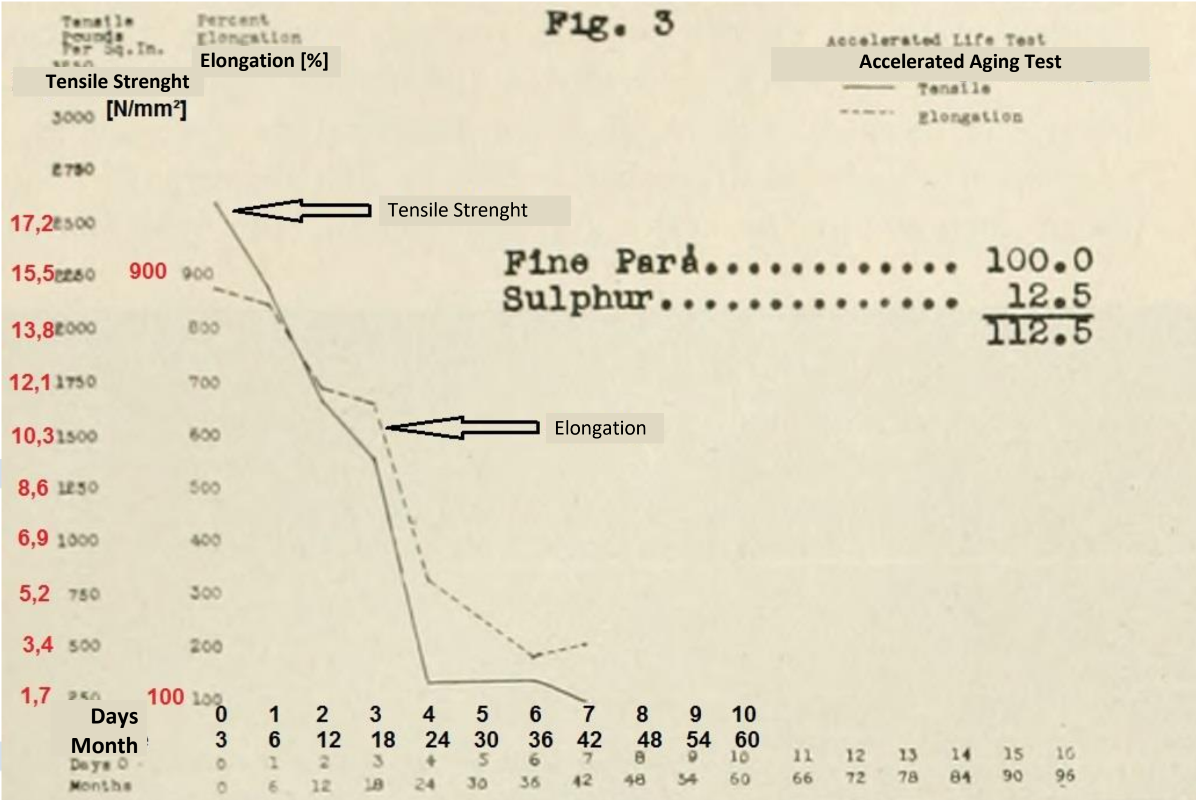

Fig. 16: Probably one of the oldest preserved heat aging curves in the world: For accelerated aging test, in the X-axis only the days are relevant. In GEER's diagrams in this 1921 publication, one day of accelerated aging is always equated to six months of hot air aging. [60] (Image from the Biodiversity Heritage Library, digitized by New York Botanical Garden, LuEsther T. Mertz Library, www.biodiversitylibrary.org, edited and supplemented by O-Ring Prüflabor Richter)

Fig. 17 examines the same compound with the same cross-linking time as in the previous figure (**Fig. 16**), only at a different time and on different test specimens. The dotted line shows the natural aging at room temperature in a dark room over a period of five and a half years. Only the tensile strength parameter is compared. With this diagram, GEER wanted to show that his test was somewhat "sharper" than natural aging, but that the two curves are similar in shape.

[60] GEER, William C. und EVANS, Walter, W.: Ten Years‘ Experience with Aging Tests in: India Rubber World,1September 1921, S. 890 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050939)

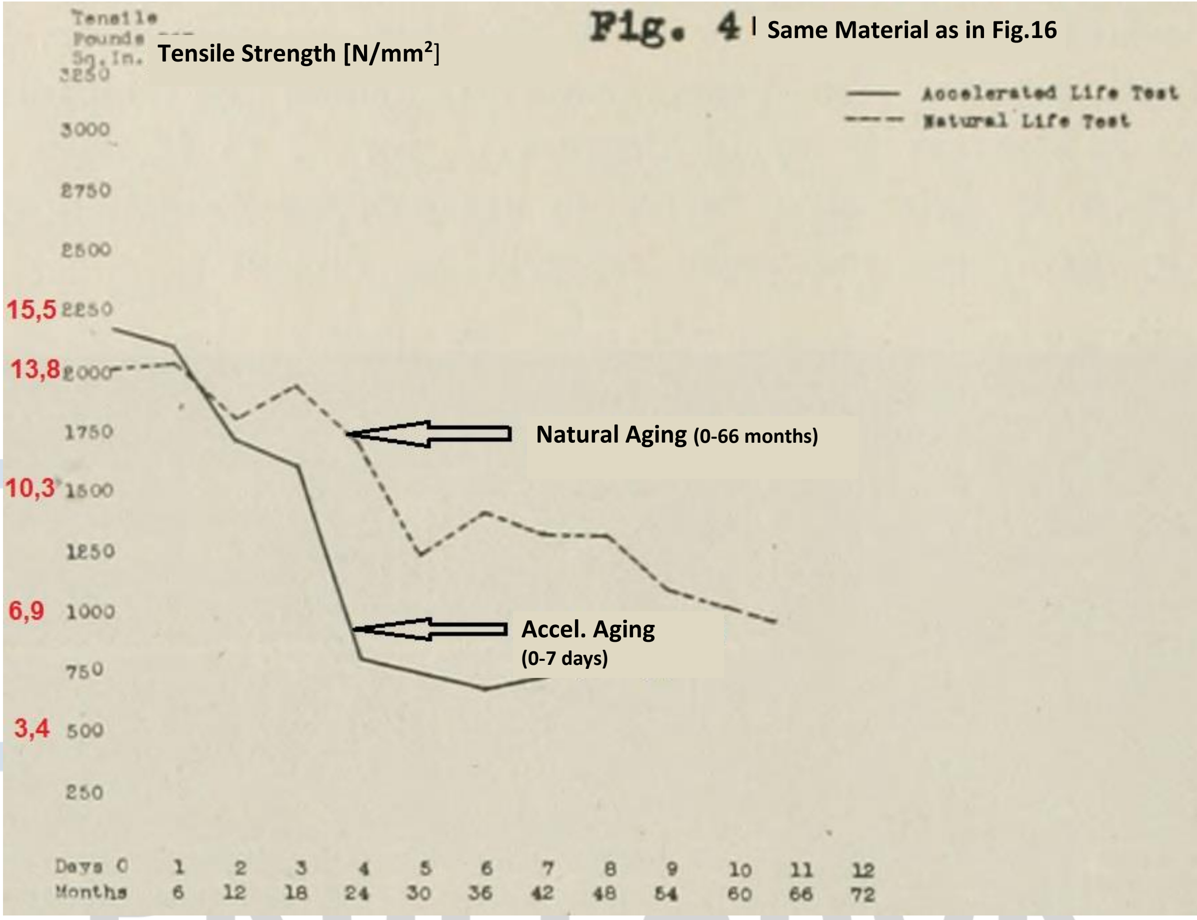

Fig. 17: Same compound as in the previous diagram, here a comparison of natural and accelerated aging[61] (image from the Biodiversity Heritage Library, digitized by New York Botanical Garden, LuEsther T. Mertz Library, www.biodiversitylibrary.org, edited and supplemented by O-Ring Prüflabor Richter)

The following **Figs. 18 and 19** show a poor and very good compound considering the conditions at the time.

The picture can be viewed under the following link: http://biodiversitylibrary.org/page/7050939 (see Fig.5)	The picture can be viewed under the following link: http://biodiversitylibrary.org/page/7050939 (see Fig.6)

Fig. 18: Example of a poor compound (only results from heat aging over 14 days at 70°C, solid line = tensile strength, dotted line = elongation at break, Y-axis classification as in Fig. 16)[62]

Fig. 19: Example of a very good compound (comments on the left)[63]

[61] GEER, William C. und EVANS, Walter, W.: Ten Years‘ Experience with Aging Tests in: India Rubber World,1September 1921, S. 890 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050939)
[62] Ebd., S. 890
[63] Ebd., S. 890

In the following **Fig. 20**, a compound of an older type is presented again, which uses litharge as an accelerator. The heat aging test is again sharper than natural aging. GEER and EVANS generally found that compounds that remained almost constant in tensile strength over the first three or four days of heat aging and showed no significant decrease in strength values thereafter, normally performed better in natural aging than in heat aging.

The picture can be viewed under the following link: http://biodiversitylibrary.org/page/7050939 (see Fig.7)

Fig. 20: Comparison of the decrease in tensile strength during natural aging (dotted line) and heat aging (continuous line) over 54 months and 12 days respectively [64]

Already at the turn of the last century, there was an intensive search for possibilities to determine the optimal degree of cross-linking. The following four figures show one and the same mixture with increasing cross-linking time. The first of the four illustrations are intended to illustrate the problem with outliers. GEER and EVANS write that they do not evaluate seemingly low values because they can lead in the wrong direction. It is also interesting to note that as the degree of cross-linking increases, the curves of natural and accelerated aging come closer and closer together. They wanted to prove that heat aging is the ideal method for determining the degree of cross-linking.

The picture can be viewed under the following link: http://biodiversitylibrary.org/page/7050939 (see Fig.10)

Fig. 21: Decrease in tensile strength during natural aging (dotted line) and heat aging (continuous line), shortest cross-linking time. The low value of natural aging during day six (dotted line) is an outlier[65]

The picture can be viewed under the following link: http://biodiversitylibrary.org/page/7050940 (see Fig.11)

Fig. 22: Same compound as Fig. 21, but slightly longer curing time [66]

The picture can be viewed under the following link: http://biodiversitylibrary.org/page/7050940 (see Fig.12)

Fig. 23: Same compound as Fig. 21, but with even longer cross-linking time than Fig. 22[67]

The picture can be viewed under the following link: http://biodiversitylibrary.org/page/7050940 (see Fig.13)

Fig. 24: Same compound as Fig. 21, but with the longest crosslinking time[68]

[64] Ebd., S. 890
[65] Ebd., S. 890
[66] Ebd., S. 891
[67] Ebd., S. 891
[68] Ebd., S. 891

The last representation is a form that we are more familiar with today. A tensile elongation diagram of a tire tube mixture (rubber, sulfur, accelerator) is presented. This is a lower quality compound.

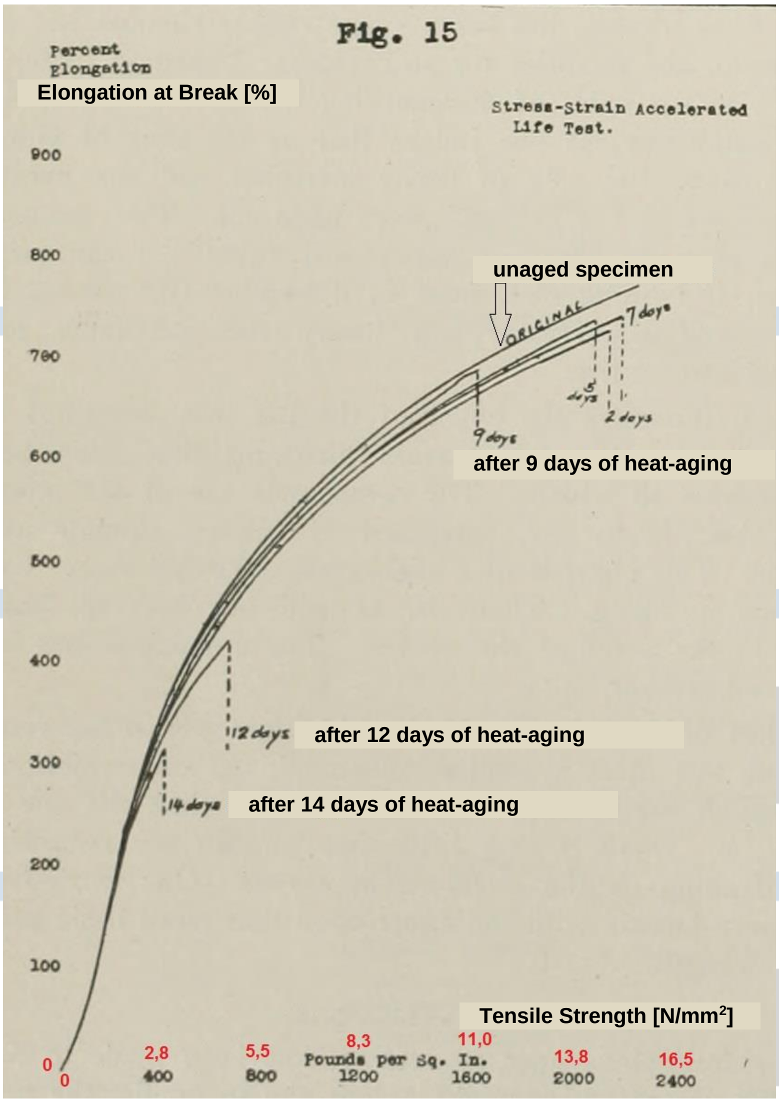

Fig. 25: Tensile elongation diagram of a low-quality, heat-aged tire tube mixture. The maximum aging time was 14 days. Especially after a longer storage duration, the tensile strength and elongation at break decrease considerably.[69] (Image from the Biodiversity Heritage Library, digitized by New York Botanical Garden, LuEsther T. Mertz Library, www.biodiversitylibrary.org, edited and supplemented by O-Ring Prüflabor Richter)

GEER and EVANS have been using the GEER test in the form shown above since about 1909. In 1921 they summarized their experiences in eight theses. These all refer to the heat aging of natural rubber. Nevertheless, a few conclusions are given to show the technical development:

[69] Ebd., S. 892

GEERS and EVANS Conclusions on Heat Aging (1921)[70]	Comments from Today's Perspective (2016)
"(1) We consider it more reliable to plot the curves and compare them than to consider the percentage deterioration from the original tensile strength.	In most test specifications today only numerical values and percentage degradation values are required. In the meantime, heat aging and tensile testing have become a well reproducible method so that there is less and less need to interpret a curve with possible outliers.
[…] (6) Most important. We are convinced that in the vast majority of cases of deterioration of rubber compounds happening too rapidly is due to over or undercure, and chiefly overcure, rather than to any one or more compounding ingredients. This life test with us has been of utmost value in leading us to correctness of cure.	That is no longer valid today. The aging resistance of elastomers can be considerably extended, for example, with antioxidants. (The first antioxidants were developed between 1910 and 1920.)
[…] (7) This test is a comparative and not an absolute one and should never be used to compare compounds of different type.	Today, comparisons are possible, but asking the right questions is crucial. This is the basis of specifications that are used to compare products from different manufacturers.
[…] (8) When used properly, there has been found to be an approximate correspondence between short-life and natural-life test, […]"	Today, natural aging is no longer as important as it used to be in GEER's time, as many applications take place in elevated temperature ranges and "aging master curves" can be created with simplified Arrhenius multipliers.

Tab. 2: Theses on heat aging by GEER and EVANS from 1921, commented from today's perspective

6. Further Development of Accelerated Aging and Current Testing Practice

6.1 Accelerated Aging Tests Developed After 1916 and Their Application Today

After GEER's oven test, further accelerated oxidative aging tests - related to aging in the heating cabinet - were introduced:

- The oxygen bomb according to BIERER-DAVIS (**Figs. 26 and 27**) from 1924[71] was introduced, among other things, because the test times in the classic GEER test at 70°C became too long due to technical further development (although still of NR

[70] GEER, William C. und EVANS, Walter, W.: Ten Years' Experience with Aging Tests in: India Rubber World,1September 1921, S. 892 (Weblink zu dieser Seite: http://biodiversitylibrary.org/page/7050941)
[71] BIERER, J.M. und DAVIS, C.C.: An Improved Rubber Aging Test Involving Oxidation under Pressure in: Industrial and Engineering Chemistry, Vol. 16, July 1924, S. 711-717

mixtures). It was also very helpful in the development and rapid testing of antioxidants. The valid DIN 53508 (March 2000 edition, subsections 4.2, 6.5 and 7.2.2) still describes aging in pressure chambers according to Bierer-Davis (preferably test conditions according to DIN: oxygen pressure (21±1) bar at (70±1) °C above (24+0/-2) h or an integer multiple). In the German technical literature of the 1960s, this method can still be found more often, but it is no longer relevant in today's testing practice. Even with this new test method, the temperature seems to have been varied only in the range between 60° and 70°C. As a result, "vulcanizates based on synthetic elastomers which age too slowly under the conditions of the Bierer Davis test, (...) had to be subjected to the Geer test at 100°C to 125°C or above".[72] In addition, this method presented the risk of spontaneous ignition or explosion and "the disadvantage of a too rapid oxygen attack, so that there was a clear and recognizable oxidation gradient within the mass [of the test specimen]". [73] This was also visible on the surface of the test specimens.

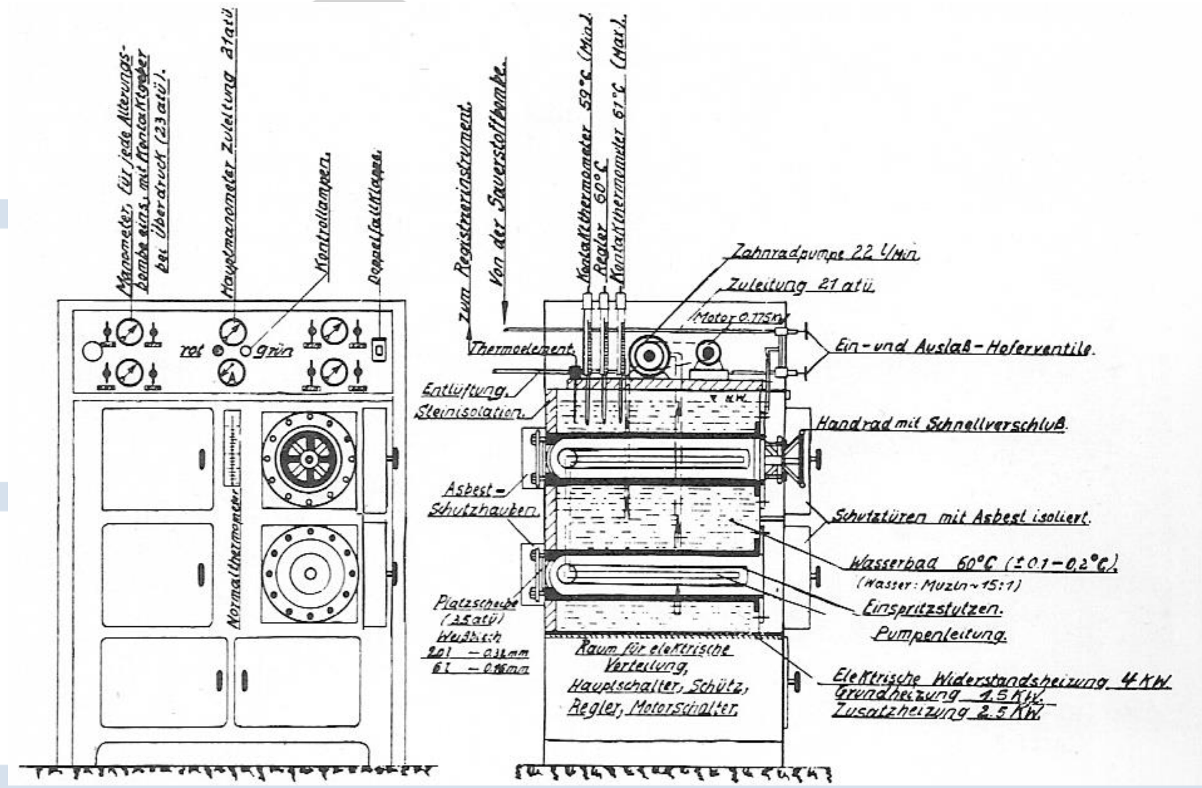

Fig. 26: Schematic sketch of an "oxygen bomb" test system according to BIERER-DAVIS [74]

Comparisons of aging according to GEER and BIERER-DAVIS can only be found in older literature[75], e.g. in the book "Kautschuk und verwandte Stoffe" from 1940:

---

[72] KEMPERMANN, Th.: Alterungsschutzmittel in BOSTRÖM, S (Hrsg.).: Kautschuk-Handbuch , Band 4, Stuttgart, Verlag Berliner Union, 1961, S. 368

[73] DUFRAISSE, Charles: Autoöxidation and Deterioration by Oxygen Proöxygens and Antioxygens in: DAVIS, Carroll, C. und BLAKE, John T. (Hrsg.): The Chemistry and Technology of Rubber, Reinhold Publishing Corporation, New York, 1937, S. 495

[74] ECKER, R.: Mechanische-technologische Prüfung von Kautschuk und Gummi in: BOSTRÖM, S (Hrsg.).: Kautschuk-Handbuch , Band 5, Stuttgart, Verlag Berliner Union, 1962, S. 179

[75] BOSTRÖM, S.; LANGE, K.; SCHMIDT, H.; STÖCKLIN, P.: Kautschuk und verwandte Stoffe – Eigenschaften und

The diagrams shown on page 432f very clearly show the superior aging resistance of the synthetic polymers tested here (perbunan (=NBR), buna S (=SBR) and buna 85 (=BR)) compared to natural rubber: In the first diagram, which shows the synthetic polymers with natural rubber at a GEER heat aging at 70°C (0-32 days), one can clearly see the faster decrease in the strength of the natural rubber due to aging compared to the synthetic elastomers, which suggests more than double the service life of the synthetic elastomers.
In another diagram, the elongation at break of the above-mentioned materials after GEER heat aging (0-32 days at 70°C) is compared. Surprisingly, the clear differences described above cannot be recognized so obviously in the evaluation of the elongation at break. This only becomes more evident after approx. 24 days at 70°C.
In a third diagram, the four materials are tested in a Bierer-Davis bomb at 60°C (0-32 days). Hereby the Bierer Davis Bomb delivers already at 60°C and after eight days show clear results for tensile strength and elongation at break regarding the superiority of synthetic polymers. This test method according to BIERER-DAVIS would certainly still be an interesting approach today for shortening test times, but in terms of safety it would be much more difficult to implement than heat aging. ASTM D 572 still describes this test method today (T=70 bar, p= 21 bar), but with a corresponding warning (1.3). However, this test hardly appears in today's specification tests of elastomers. Users are more likely to tolerate test times of 1-6 weeks in order to obtain sufficient information on the heat resistance of a compound.

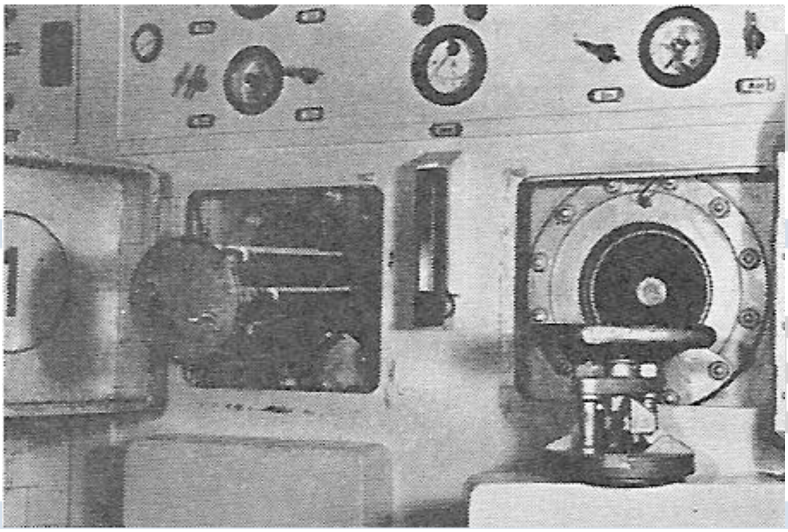

Fig. 27: "Oxygen bombs" test system according to BIERER-DAVIS, around 1960 [76]

- **The air bomb according to BOOTH** [77] (**Fig. 28**) from the year 1932 appears in the German specialist literature in the 1960s, probably in a slightly more modified form still: "The fastest aging is carried out in the bomb filled with compressed air of 5at (unit) at 127°C. However, it is more the heat resistance that is tested. The stress duration is

Verarbeitung, Union Deutsche Verlagsgesellschaft Roth & Co., Berlin, 1940, S. 432
[76] ECKER, R.: Mechanische-technologische Prüfung von Kautschuk und Gummi in: BOSTRÖM, S (Hrsg.).: Kautschuk-Handbuch , Band 5, Stuttgart, Verlag Berliner Union, 1962, S. 179
[77] BOOTH, E.W.: Heat-Resisting Inner Tube Stocks in: Industrial and Engineering Chemistry, Vol. 24, May 1932, S. 555-559

usually three hours or a multiple of three hours". [78] In the USA in the 1950s, however, the air bomb was used less frequently than the geothermal furnace or the oxygen bomb.[79] This method was an attempt to replace the oxygen bomb which had become too slow in the meantime.[80] However, as already described above, by using the GEER method at higher temperatures, acceptable test times could be achieved again.

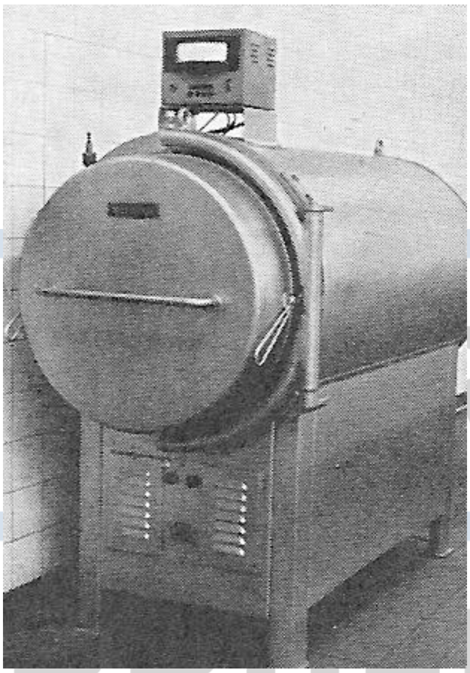

Fig. 28: "Compressed air or hot air bomb" testing system, around 1960 [81]

- The **"water bomb" according to GILLMAN and HAINES**[82] was an attempt to reduce the testing period again multiple times. Instead of storing the specimens in oxygen or air, they were stored in a strongly oxidizing liquid (e.g. potassium chlorate) in autoclaves under pressure. Supposedly, a three-hour storage in the "water bomb" corresponded to an eight-day storage in an "oxygen bomb".[83] Today, there is a rather skeptical view of such extreme short-term tests for reproducing service life stresses, as the uncertainty of the results is simply too great when they are applied to the logarithmic scale (e.g. when evaluating by means of the Arrhenius equation).

- **Cell-type ovens:** The first ASTM D865 standard, which exclusively describes aging in cell-type ovens, was published as early as 1946. The technical basis for an ISO

[78] Translated from ECKER, R.: Mechanische-technologische Prüfung von Kautschuk und Gummi in: BOSTRÖM, S (Hrsg.).: Kautschuk-Handbuch , Band 5, Stuttgart, Verlag Berliner Union, 1962, S. 178
[79] Vgl. JUVE, A.E.: Physical Test Methods and Polymer Evaluation in: WHITBY, G.S. (Hrsg.): Synthetic Rubber, John Wiley& Sons, Inc., New York, 1954, S. 439
[80] Vgl. MAASEN, G.C.: Introduction in: Symposium on Aging of Rubbers, Chicago Spring Meeting ASTM Special Technical Publication No. 89, March 1949 S. 1
[81] ECKER, R.: Mechanische-technologische Prüfung von Kautschuk und Gummi in: BOSTRÖM, S (Hrsg.).: Kautschuk-Handbuch , Band 5, Stuttgart, Verlag Berliner Union, 1962, S. 179
[82] GILLMAN, H.H. und HAINES, W.H (Jr.): A water bomb for studying the oxidation of Elastomers in: Rubber Age (N.Y:), 71, 1952, S.767-771
[83] Vgl. BUIST, J.M.: Aging and Weathering of Rubber, herausgegeben von: The Institution of the Rubber Industry, W.Heffer & Sons Ltd., Cambridge, 1956, S. 82

standard was defined at a meeting of the ISO Technical Committee 45 in Düsseldorf (Germany) in the 1950s.[84]

Already early (1947) a better reproducibility between laboratories was described in the literature in comparison to furnace aging.[85]

This method can be found in our laboratory practice today, even if on a very small scale and for special applications (e.g. avoidance of contamination of different elastomer specimens). Tests in glass tubes (cell-type ovens) according to ASTM D865 count less than 1% of our heat aging tests compared to furnace aging according to GEER (ASTM D573, ISO 188 and DIN 53508).

Tests have also been developed to highlight specific aging factors, such as ozone, UV, light, relaxation, humidity and steam tests. In the automotive industry, outdoor parts are still exposed to the effects of dry and hot humid climates (e.g. Arizona and Kalahari tests). This also equates a realistic time-lapse test in which about one year of exposure should correspond to the service life of the component.

There were also tests to determine the oxygen absorption, e.g. the manometric method according to DUFFRAISE. [86]

6.2 Why Has Geer-Test Established Itself Today as the Standard Test Method for Heat Aging?

- Easy to use and relatively inexpensive, little equipment required and no chemical expertise or chemical laboratory required, can be implemented in areas with general "mechanical engineering knowledge" (e.g. in mixing, production etc.)
- Correct temperature (Geer chose 70°C for the standard NR, which was not too high as in other aging tests of his time). If the temperature is too high, there is a risk of non-homogeneous aging across the cross-section, and if the temperature is too low, the test times required are too long.
- As early as 1916, GEER recommended testing on a comparative basis, which means testing relatively (unaged, aged) instead of referring to absolute values of certain standard compounds (very practice-oriented approach). Of course, this approach was also adopted in other test methods, so that this is not a unique characteristic of aging according to GEER.
- Favorable time of origin (from the middle of the 19th century until the beginning of the 20th century, all essential physical basic test methods for elastomers were established. For example, ShoreA is not the best spring pressure method for hardness measurement, but was introduced in 1915 and was therefore already so established that better alternatives could no longer prevail later on)
- The Geer-Test could be well adapted to other synthetic polymers by only increasing the temperature, first to 100°C, later even higher.

[84] ECKER, R. und BRÄUTIGAM, C.: in: Kautschuk und Gummi, 8, 1955, S.269ff.
[85] JUVE, A.E. und BOXSER, H. et al. In: ASTM Bulletin No. 147, 1947, S. 51-53
[86] LE BRAS, Jean: Grundlagen der Wissenschaft und Technologie des Kautschuks, Verlag Berliner Union, Stuttgart, 1956, S. 317f.

- No special safety precautions or special gases necessary, as for example with the oxygen bomb according to BIERER-DAVIS.
- Universally applicable test apparatus: the heating chambers can be used not only for air storage, but also for medium immersion (with or without autoclave) and compression set tests.

6.3 What is What? Attempt to Classify and Structure Various Parallel German and English Terms in the Context of Aging.[87]

Because of many different standards and manufacturers of laboratory furnaces, various similar technical terms are used in literature. This overview, which does not claim to be exhaustive, provides an initial orientation for the interested reader:

Generic Term	German	English
Heat Aging	• Künstliche Alterung (DIN 53508) • Alterung in Heißluft • Beschleunigte Alterungsprüfung • Alterungsprüfung (Wenn ohne Zusatz ist meist Heißluftalterung gemeint) • Alterung bei erhöhten Tempe-raturen • Oxidative Alterung	• Heat aging • Accelerated Aging (ISO 188) • Deterioration by air at an elevated temperature (ISO 188) • Deterioration in an Air Oven (ASTM D 573) • Oxidative and thermal aging (ASTM D573 in the current standard test) • Oxidative Aging • Aging at elevated temperatures • Heat-resistance test (technical literature)
Cabinet Oven	• Wärmeschrank (DIN 53 508) • Standard Ofen • Geerofen (bis in die 1960er Jahre in Deutschland häufig verwendet) • Umluftofen • Kabinettofen • Heißluftofen • Alterungsofen • Ofen	• Air oven (ASTM D573) • Cabinet oven (ISO 188: The ISO uses "air oven" as an umbrella term for "cabinet oven" and "cell-type oven".) • Geer oven (still in use today in English literature)
Cell-Type Oven	• Zellenofen (DIN 53508)	• Deterioration by heating in air (test tube enclosure) (ASTM D 865)

[87] Chapters in extracts taken from: BLOBNER, Ulrich und RICHTER, Bernhard: Fachwissen Prüfverfahren für Elastomere: Heißluftalterung von Elastomeren – Prüftechnische Grundlagen und wissenswerte Besonderhei-ten, 06/2015, Internetveröffentl.: http://www.o-ring-prueflabor.de/files/fachwissen_hei__luftalterung_06_2015.pdf

		• Metal block type aging oven (ASTM D865 Subheading for a cellular furnace with a metal block as heat transfer medium) • Cell-type oven (ISO 188) • Cell aging ovens (technical literature) • Multi-cell aging oven (technical literature)

Tab. 3: Comparison of different technical terms with the same or related meanings in German and English with regard to the thermal aging of elastomers

6.4 Conclusions of Hot Air Aging According to GEER Today [88]

With the help of heat aging according to GEER, the following points are examined in today's laboratory practice:

- Heat resistance of a material (short-term and long-term heat resistance (>168h)): Assessment of property changes before and after storage (tensile test, hardness, volume, etc.). In the early days of the elastomer industry, the results of GEER aging were usually compared with so-called "shelf aging" specimen, since most elastomer products were only used in ambient air. In the meantime, many applications take place at elevated temperatures, so that heat aging is closer to reality than classic natural "shelf aging".[89]
- Lifetime predictions (determination of an isothermal equivalent stress with simplified Arrhenius multipliers or the RGT rule / and/or with the definition of a lifetime criterion, e.g. relative change of elongation at break by 50% or achievement of a compression set of 80%)
- Information on compound and processing quality (e.g. admixture of antioxidants, conclusions about the cross-linking system, suitable plasticizers)
- Determination of material characteristics for numerical calculations

Other effects/influencing factors besides oxidation during GEER heat aging:

- Outgassing of volatile components (e.g. plasticizers) which are removed by the flow in the hot-air oven (= mostly undesirable effect)

[88] More detailed information on this question can be found in: BLOBNER, Ulrich und RICHTER, Bernhard: Fachwissen Prüfverfahren für Elastomere: Heißluftalterung von Elastomeren – Prüftechnische Grundlagen und wissenswerte Besonderhei-ten, 06/2015, Internetveröffentl.: http://www.o-ring-prueflabor.de/files/fachwissen_hei__luftalterung_06_2015.pdf
[89] Vgl. JUVE, A.E.: Physical Test Methods and Polymer Evaluation in: WHITBY, G.S. (Hrsg.): Synthetic Rubber, John Wiley& Sons, Inc., New York, 1954, S. 442

- Exchange of volatile components (cross-contamination), critical in the storage of different mixtures (= undesirable effect), in critical cases it must be avoided on cell-type ovens
- In case of carelessness or unawareness: Presence of rubber poisons (e.g. copper, manganese) in the oven (e.g. when storing more complex finished parts)
- Precise temperature control is required for reproducible results

6.5 Today's Improvements of the GEER Method

Interestingly, there is no significant point in the original method described in 1916 that has been technically outdated or wrong. The decisive improvements of the last 100 years relate only to the precision of the procedure and the evaluation of results.

- Worldwide exact standardization of the process (ISO, ASTM and national standards)
- Electrical temperature control and monitoring of the oven temperatures
- Better ways to control and check air changes and flows (laminar, turbulent)

7. What Remains of Dr. William Chauncey Geer?

7.1 Possible Traces of the "Geer Test" in Current Standards

In the previous chapters, many details of the GEER method have already been addressed, which are still found today in many specifications for heat aging.
In the current DIN 53508 (March 2000), however, an interesting "fossil" can still be found: The 7seven days at (70±1)°C, which have become rare in the meanwhile, are given as the preferred test conditions in Chapter 7.2.1. A combination that reminds us of a great pioneer and ground-breaker of modern elastomer testing: Dr. William Chauncey GEER.

7.2 What Can We Learn from William C. Geer Today?

- Success of scientific work in industry: practical relevance and simple method
- Modesty in the presentation of his results
- Many test methods today are too detailed and the modern data processing leads to trust the numbers of a computer too much instead of questioning them again and again and not losing sight of the essential boundary conditions of a test method.
- The historical view helps us to ask the basic questions once again to find out why some test methods have proven themselves for so many years.
- University research has its justification, but for the industry, in particular, a laboratory service is essential that can reproduce standard test methods and, very importantly, explain them in detail to the customer so that conclusions can be drawn for practical

use based on the measured values. William C. Geer understood this practical relevance.

At the Goodyear Rubber Awards ceremony in 1951, GEER gave a speech on "Strategy in Rubber Research". In it, he describes at the beginning of his career in 1908, the rubber industry was highly secretive and competitive. Early on, he realized that it was important to have interactions between experts from different companies, not to exchange secret processes or compound compositions, but to solve common and difficult problems. "The common [problem] was the key to forming acquaintances, friendships and mutual trust."[90] This cross-company cooperation was also very valuable for the enormous development and manufacturing challenges in the two world wars.
In his book "The reign of rubber", his enthusiasm for rubber as a material, but also his strength and courage to have visions and to put them into practice become tangible in his concluding sentences: "The dreams of today become the realities of tomorrow; possibly, often not in the same form in which they were originally dreamed, but nevertheless the dream made the suggestion. This intense activity will result in articles of increased value and service to the consumer. Rubber is a substance which, in its ramifications extend by the forces of investigation, will certainly serve humanity in many forms than in does today"[91]

8. Acknowledgement

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[90] GEER, William C.: Goodyear Rubber Award Address: Strategy in Rubber Research in: Industrial & Engineering Chemistry, Nov. 1951, Vol. 43, S. 2438
[91] GEER, William C.: The reign of rubber, The Century company, New York, 1922, S. 339f. (Diese Buch ist online abrufbar: https://archive.org/details/reignofrubber00geer)