NEW OPTICAL GLASSES

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BEFORE 1880 the only types of optical glass available to lens designers were the flint-crown series, in which the addition of progressively increasing amounts of lead oxide led to a progressive increase in both refractive index and dispersive power, so that in effect there was a fixed relation between the dispersive power and refractive index of all available glasses (Fig. 1).

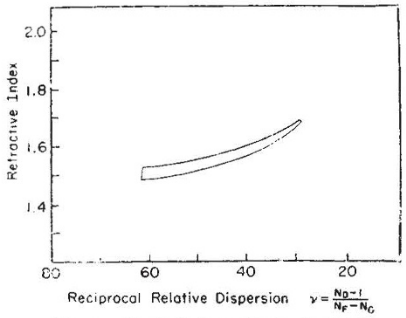

Fig. 1. Optical glasses (prior to 1880)

In order to achromatize any lens, the positive elements must be of lower dispersive power than the negative elements, and in those days this meant that the refractive index of the positive elements had to be low, and that of the negative elements high. This had two very adverse effects: on one hand, it tended to make the Petzval sum large, giving a strongly inward-curving field; and, on the other hand, it made the surfaces of the positive elements strong and those of the negative elements relatively weak. As the lens on the whole is positive, this resulted in considerable amounts of zonal spherical aberration, and also indirectly in large residuals of all the other aberrations.

For two reasons, then, a crown glass was needed with low dispersion and high refractive index, and also, if possible, a flint glass of high dispersion and low refractive index. The invention of barium crown glass in the 1880's by Abbe and Schott helped greatly to meet the first requirement, but the problem of the low-index flint was not solved at that time. (Incidentally, plastics, crystals and liquids mostly tend to have higher dispersion for their index than glasses, but these materials are generally undesirable for other reasons.)

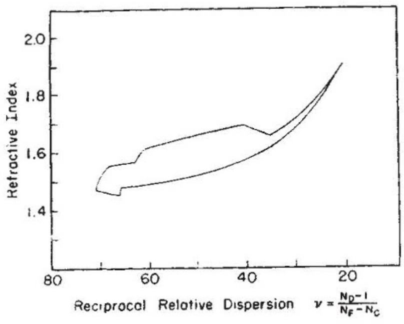

Fig. 2. Optical glasses (prior to 1934)

With the introduction of barium crown glass, many new types of photographic lens became possible, the first to be developed being cemented triplets of the 'Dagor' type, in which the three glasses are common crown, light flint, and dense barium crown in that order. Barium crown glass also greatly improved all lenses of the air-spaced type (the Cooke triplet and the 'Celor', for example) by weakening the surfaces of the crown elements and enabling the designer to shorten the lens without adversely affecting the Petzval sum. To be sure, some successful lenses of the meniscus type, for example, the 'Omnar', were designed without using barium crown; but these were the exceptions, and they did not become very popular.

The refractive index of barium crown glasses was raised slowly and steadily by Schott until the early 1930's (Fig. 2). At that time they introduced *SK*-16 and *SK*-18, which marked the upper limit of the ordinary barium–soda–lime silica types. These glasses are chemically unstable and present difficulties in lens manufacture because of their susceptibility to acid staining, and because of their brittleness.

Following the First World War, G. W. Morey, who had done work of great value in connexion with the production of optical glass for military purposes, discussed the advances which could be made in optical glasses with C. W. Frederick, chief of the lens designing bureau of the Eastman Kodak Company. Frederick suggested that what was wanted was a very high refractive index with low dispersive power and that even a small production on a laboratory scale would be useful. Morey undertook to study the optical properties of glasses in relation to chemical composition especially with a view to the production of high refractive index crown glasses. To this end all high atomic-number cations were chosen for systematic study in silicate, borate and phosphate glasses. Small melts of twenty to forty grams were made to indicate the field of glass formation. The more promising ones were repeated in larger melts of fifty to one hundred grams.

By 1933, the work had progressed to the point where silicon and phosphorus were discarded as glass-forming elements. Boric oxide had by now proved to be by far the best fluxing agent. Oxides of elements such as lanthanum and thorium found in the rare earths, and columbium, tantalum, tungsten, titanium, zirconium and strontium were used in major portions up to 80 per cent by weight, with or without the usual barium, zinc, magnesium and aluminium.

In 1934, samples of unusual glasses with characteristics n_D in the region of 1·85 and ν, the reciprocal relative dispersion, of 47·0 were in existence, and their properties well measured. About this time the work was expanded to a larger scale by the Kodak Research Laboratories. Under the direction of S. E. Sheppard, L. W. Eberlin and P. F. DePaolis made a systematic study of the solubility of the rare elements in boric acid and the limits of glass formation. The results of the combined work were revealed in patents by Morey[1] and by Eberlin and DePaolis[2].

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Lanthanum is very soluble in boric acid, and its contribution to higher refractivity without increase of dispersion is remarkable. The oxides of tantalum, thorium and tungsten are soluble in the lanthanum borate base glass in amounts up to 35 per cent. These new borate glasses are very stable and fairly hard. They are harder than flints, suitably stable to the atmosphere, and amenable to optical shop practices of moulding, grinding and polishing.

Early in the development work it was found that the new rare-element borate glasses were extremely corrosive to all known pot refractories. A decision was therefore made to use platinum for the actual production of these glasses. This was justified on the basis that no platinum would be lost by contamination, and that the glass, once homogenized, could be poured in its entirety, free from striæ, into a single slab or into cast shapes without striæ, seed, bubbles or other defects usually attending a glass made in a refractory pot.

The first of the new glasses to be made had a refractive index of 1·7445 and a reciprocal relative dispersion of 45·8. The glass was slightly yellow, but further work established the origin of the yellow colour, and finally glasses were produced as colourless and homogeneous as any other ordinary optical glass.

Pilot-plant operation began in September 1937, and the first commercial glass was delivered in June 1939. Production increased rapidly, and more than 125,000 lb. of rare-element glass were produced during the Second World War (1942–45). Much of the success of the enterprise was due not only to the platinum equipment but also to the Kodak method of using all-electric heating and a small-pot, 'multi-pot–multi-stage' process.

Under sustained production conditions during the War, the yield of finished usable glass in a cast form was 95 per cent of the theoretical glass available in the batch.

Electric heating was retained in a plant that was erected during the War and operated from December 1942 to September 1945 on a continuous basis of approximately 5,000 lb. of finished glass a month. The process consisted of feeding thirty-two 10-lb. platinum-lined pots every twenty-four hours, starting one every three-quarters of an hour, and progressively moving these pots through the various stages of the glass-making process.

Since 1940 the types of these glasses in production have been extended, and at the present time the following seven types are being made:

	n_D	ν		n_D	ν
EK–110	1·69680	56·2	*EK*–330	1·75510	47·2
–210	1·73400	51·2	–450	1·80370	41·8
–310	1·74500	46·4	–448	1·88040	41·1
–320	1·74450	45·8			

All these glasses contain thorium, and in the case of folding cameras, in which the lens may rest for a long time in close proximity to film, the radioactivity of the thorium may be a disadvantage. A thorium-free equivalent of *EK*-320 is available.

The new glasses were first used in lens design in 1934; actual production of lenses began a few years later, and to-day many of the Eastman Kodak 'Ektar' lenses contain the high-index glass. The versatility of these glasses is evidenced by the large number of lens patents which specify such glasses.

After the transfer of the production of the new glasses to the factory, the Kodak Research Laboratories continued their study of optical glasses. Theoretical considerations by M. L. Huggins and K. H. Sun predicted the possibilities of further new glasses, and their predictions have proved correct. Of the glass systems of this type which were worked out by Sun, the most useful were flint glasses containing titanium oxide and using fluorine in addition to silica.

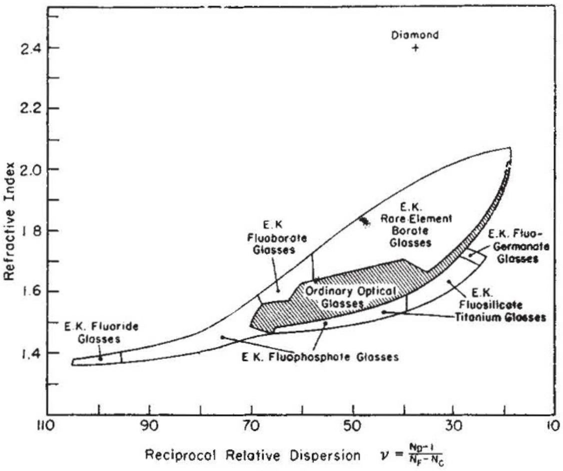

Fig. 3

These unusual glasses lie well below the ordinary flint line (Fig. 3). For a given index, the dispersion is appreciably greater than that of ordinary flints. In this sense the glasses may be termed super-flints. The best glasses lie in the region 45 per cent silica, 28 per cent titanium oxide, 27 per cent sodium fluoride, ranging in optical properties from n_D 1·65/ν29 to n_D 1·58/ν36·6. The glasses can be moulded, are very resistant to tarnish, and are easily fabricated by the usual optical methods.

The fluosilicate flints are almost as useful to the optical designer as the high-index glasses, since they extend the possible difference between crown and flint refractive index and between crown and flint dispersion. With these glasses, three-element lenses have been designed to give even better performance than the usual four-element types. K. H. Sun succeeded in producing novel mixtures in some twenty quite different glass fields, including fluo-borate, fluo-germanate[3] and fluo-phosphate systems.

A most interesting group of glasses suggested by Sun are those containing no oxides and composed entirely of fluorides. These glasses show the characteristic low refractive index and extremely low dispersion previously available only in fluoride minerals. The refractive index in most of the glasses is approximately 1·38–1·39 and the ν-value, 100. Moreover, the glasses are transparent to below 300 mμ in the ultra-violet and to 5 μ in the infra-red, so that they may be very useful in the making of instruments requiring optical transparency over a wide range of wave-lengths. Difficulties have been met in the production of these all-fluoride glasses, but it is possible that these difficulties may be overcome in the near future.

The extension of the frontiers of optical glass by this work is illustrated in Fig. 3. In this figure the range of optical glasses known before 1934 is shown shaded, while the larger area shows the glasses that can be made at the present time.

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[1] British Patent 462,304, March 3, 1937; United States re-issue Patent 21, 175, August 15, 1939.

[2] United States Patents 2,206,081; 2,241,249; 2,434,146; 2,434,147; 2,434,148; 2,434,149. British Patents 462,304; 608,298.

[3] United States Patent 2,425,403.

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