OBSERVATIONS ON THE BLEACHING OF SUNFLOWER OILS OF DIFFERENT QUALITY

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Vegetable oils have usually characteristic colours due to various lipochroms (such as carotinoides, chlorophyll, gossipol, anthocyans, etc.). Because of the different quantity of these colouring substances, as well al of their lack and surplus respectively, tomato oil for instance has a redish, rice and grapeseed oils a greenish, sunflower oil a yellow colour. Hence the colour is almost as characteristic for raw oils of different types as for instance the smell thereof or the taste and the characteristic absorbtion spectra are published in the literature for the individual oils (1).

However, the characteristic colour composition is often altered by the technology processes and this alteration may be as intensive in extreme cases that causes severe troubles at the processing and refining of the oil.

In this paper we report on such cases and also outline some observations and experiences gained at the investigation and discolouration of some sunflower oils having a more dark colour.

EXPERIMENTAL SUBSTANCES

Investigations have been carried out with three sunflower oils of different colour and origin. All three oils resulted from factory processing and were mixtures of pressed and extracted oils in a proportion of 2 : 1. There have been no differences in the manufacturing technologies of the oils, however, considerable differences existed in the quality of the grain raw materials.

1. Raw oil of light colour — raw material was Krasnodar-type sunflower grain of standard quality.
2. Raw oil of brownish colour — Krasnodar-type sunflower grain warmed up considerably during storage (70°C).
3. Raw oil of dark colour — Krasnodar-type sunflower grain which get ignited during storage.

Colour values :

Oil type	Iodine colour number	Lovibond colour number (2)		
		Yellow	Blue	Red
Light-coloured oil	15	35		3.4
Brownish oil	40	50	0.1	6.0
Dark-coloured	300*	400	1.5*	56

* Calculated value by diluting.

The warming up and ignition of the grain batches took place after a two month storage in silos due to the incomplete removal of moisture and organic impurities. Since to the best of our knowledge no literature data are available relating to the investigation of such dark coloured oils, the data of analysis thereof are given in details (table 1) (2).

Table I

Standard analysis data of the investigated oils

Analyses	Light	Dark	Brownish	Limit value according to standard (2)
	sunflower oils			
Taste, smell	A	B	C	D
Density at 20°/20°C	0.918	0.919	0.920	0.915—0.927
Refraction index at 20°C	1.4748	1.4745	1.4748	1,473—1.477
Acid number	3.4	11.6	8.4	6.0 max.
Saponification number, per cent	190.6	190.7	191.9	186—196
Iodine number	127.4	130.0	128.0	110—143
Unsaponifiable matter, per cent	0.60	0.81	0.68	1.0 max.
Peroxide number	6.0	4.2	8.3	—
Strange substance content, per cent	0.04	0.06	0.01	1.0 max.

A — characteristic of sunflower oil
B = tartish, musty
C = burnt, tartish
D = characteristic of sunflower oil, free of strange odours.

According to the data of table 1 most values of the dark-coloured oils comply with the limit values of raw sunflower oil settled by standard specifications. Differences occur first of all in organoleptic characteristics and also in the high acid number values. It is remarkable, that the peroxyde number of the dark-coloured oil corresponds with that of normal oils of better quality.

In addition to standard investigations we have also tested the fatty acid composition, the rapid rancidifying value by Swift, the benzidine number, the polymer and vitamin E contents of the oils as well as their infrared (3), ultraviolet and visible spectra (4) (table 2, figures 1 and 2).

According to the results there is practically no difference in the fatty acid composition and infrared spectra of the three oils. No extensive change occured in the effect of heat destruction. Oils of a darker colour may be considered as rather stable on the basis of rapid rancidifying investigations. However, such values could already been found with light-coloured raw sunflower oils.

Table 2

Some characteristics of the oils

Characteristics	Light-coloured	Brownish	Dark-coloured
	sunflower oils		
Fatty acid composition, per cent (5)			
C 16	5.3	5.5	5.2
C 18 : 1	3.7	3.7	3.9
C 18 : 2	26.0	23.0	22.5
C 18 : 3	64,5	67.2	67.5
Other acids	0.5	0.6	0.5
Rapid rancidifying value, houres (2)	7	5	6
Benzidine number (6)	0.2	2.0	3.8
„Polymer"-test (7)	negative	negative	negative
Vitamin E content (δ/g) (8)	480	450	370

No detectable polymer compounds could be found in the oils by means of the isopropyl alcohol method. Benzidine numbers are higher, however, vitamin E contents are lower in dark-coloured oils.

Visible spectras of the oils differs considerably from each other. Only absorptions of the brownish and light-coloured oils are given in figure 1 since dark-coloured oil has a very strong absorption. For this reason the absorption of their 15 percent solutions in hexane has been also tested (figure 2).

The differences of values are clearly seen on the curves particularly with respect to the dark-coloured oil.

Also differences may be found between the ultra-violet spectras first of all in the triene region, however, smaller as in the case of visible spectras (figure 3). In order to demonstrate the differences, in table 3 extinction values of all three oils at the diene and triene absorptions places are given.

Table 3

Extinction values of the tested oils in the diene and triene band $\left(E_{1\ cm}^{0,25\%}\right)$

Oil type	232 mμ	268 mμ
Light-coloured oil	1.32	0.11
Brown-coloured oil	1.22	0.18
Dark-colored oil	1.46	0.40

According to the summarized results of our investigations no significant structure changes are taking place in the oils due to heat effects exerted into the grains during storage and this could be confirmed by our experiments.

Sunflower oil of Krasnodar-type has been cracked in the laboratory by heating in a flask in order to reproduce colour, the cracked grains have been extracted by hexane. Thus a thick, black extract of cracked smell has been formed, 0.1 percent of which has been added — upon visual estimation — to the light-coloured oil

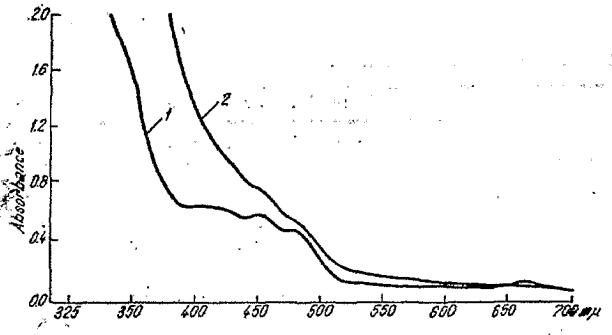

Fig. 1 — Absorption of the oils in the visible region:
1 — light-coloured oil; *2* — brownish oil.

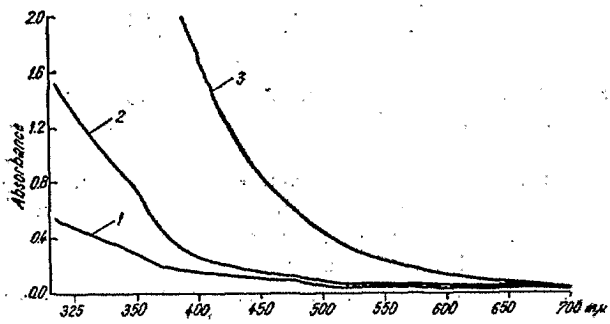

Fig. 2 — Absorption of the solutions of the oils in the visible region:
1 — light-coloured oil; *2* — brownish oil; *3* — dark-coloured oil (all oils in 15% hexane solution).

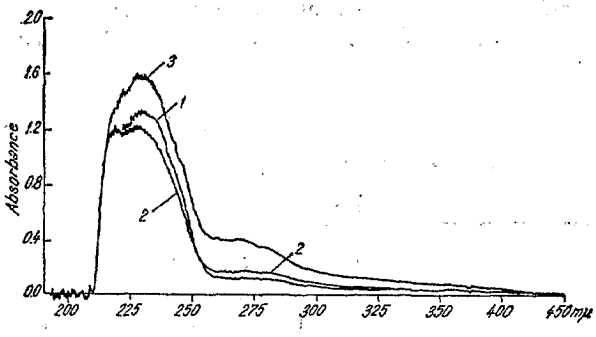

Fig. 3 — Absorption of the oils in the ultra-violet region:
1 — light-coloured oil; *2* — brownish oil; dark—coloured (all oils in 0,25% cyclo-hexane solution).

and we obtained an oil of the same grade as the brown-coloured one, by adding 0.9 to 1.0 percent the oil obtained was similar to the dark-coloured one.

This shows that, relatively small amounts of a „strange substance" may cause considerable changes of the appearance and if only small quantities of cracked grains are admixed to grains of normal quality, the oil exhibits quite changed organoleptic pecularities and other characteristics.

Note : increase of the acid number during storage was a consequence of lipase effect, however, this effect is not accompanied with the deterioration of colour in most cases.

Further on we investigated the possibilities of removing such colouring substances by disacidifying bleaching processes in order to obtain refined products of adequate quality and colour from dark-coloured oils.

METHOD FOR THE REMOVAL OF THE COLOURING SUBSTANCES

Settled oils have been disacidified at 80°C with 20 B° caustic soda solution in a laboratory mixing device (25 percent excess of caustic soda), separated on a laboratory centrifugal machine, washed and dried in vacuum.

Dried oils have been bleached in a laboratory mixing apparatus (CO_2). Bleaching temperature was 90 to 95°C, the mixing time was 20 minutes in all cases. Tonzil St bleaching earth and Decolor A active carbon have been used in the clearing process (water contents 7.3 percent and 6.8 percent respectively).

The degree of colour change has been determined by the iodine colour number, the Lovibond colour number as well as by Pons, Kuck, Frampton colour-index values (9).

It turned out namely at the testing of mixture made of light and dark coloured sunflower oils by known weight proportions that, inside the 400 to 500 mμ region the area below the absorption line is in a close relationship with the mixing proportions and colour intensities of the oils (figure 4), however, indices obtained could well be utilized also in other cases at the evaluation of sunflower oils of different colours.

RESULTS OF EXPERIMENTS FOR THE REMOVAL OF THE COLOURING SUBSTANCES

Results of neutralization and bleaching are given in figures 5, 6 and 7.

The gradual reducing effect of these procedures upon the colour indices is well visible. The lowest line in figure 5 shows for comparison the absorption line of a very light and deodorized (iodine colour number 3) sunflower oil.

The degree of bleaching was determined by direct spectrophotometric measurements with light-coloured and brownish oils, however, that of dark-coloured oil in a 15 per cent hexane solution because of its high extintion value (figure 7). Size of the area below the absorbtion line was calculated from the data of figures ; degrees of colour removal are given with areas taken as 100 in case of raw oils and disacidified oils.

These results are summarized in table 4 and figures 8 and 9. From the results the following conclusions may be drawn :

— under our testing conditions the colouring substances of dark-coloured sunflower oils may be removed by neutralization to a greater extent than those of light-coloured oils ;

— this considerable improvement of colour enables the large scale bleaching of dark-coloured sunflower oils with acceptable quantities of bleaching earth (1 to 3 per cent), in accordance with standard specifications ;

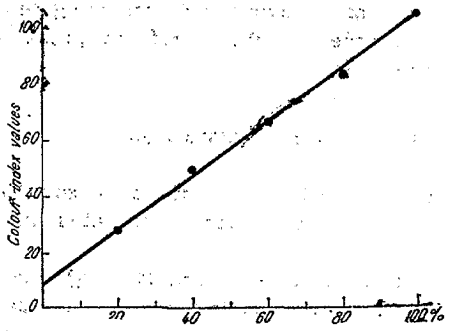

Fig. 4 — Relationship between the weight proportions of mixtures of dark and light oils and the colour indices.

Table 4

Degree of colouring substance removal

Oil type	Amount of removed colouring substances, %					
	Neutralization	Bleaching				Bleaching material
		0.5%	1.0%	2.0%	3.0%	
Light-coloured oil	20*	39	53	73	—	Bleaching earth
		24	41	66		
Brown-coloured oil	35*	52	59	68	—	„
		27	35	52	—	„
Dark-coloured oil	59	68	74	79	—	„
		22	35	47	—	„
	59		73	82	88	Bleaching earth +20% Decolor
			34	56	71	„

* Calculated on raw oil
** Calculated on neutralized oil

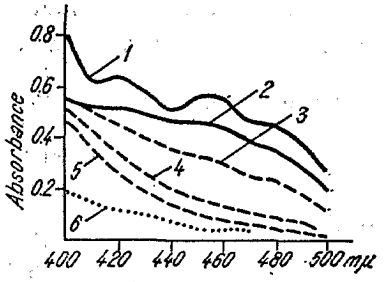

Fig. 5 — Results of discolouring of a light-coloured oil:

1 — raw oil; *2* — neutralized oil; *3* — bleached oil 0.5% bleaching earth; *4* — bleached oil 1.0% bleaching earth; *5* — bleached oil 2.0% bleaching earth; *4* — bleached oil 1.0% bleaching earth; *5* — bleached oil 2.0% bleaching earth; *6*. deodorized oil.

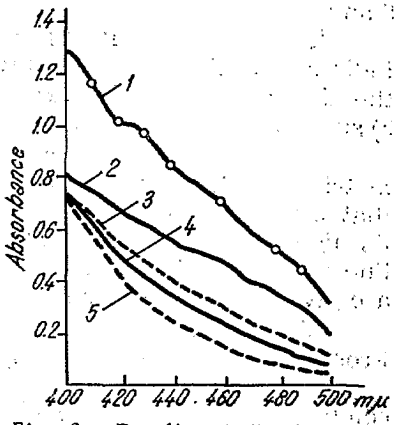

Fig. 6 — Results of discolouring of a brownish oil:

1 — raw oil; *2* — neutralized oil; *3* — bleached oil 0.5% bleaching earth; *4* — bleached oil 1.0% bleaching earth; *5* — bleached oil 2.0 % bleaching earth.

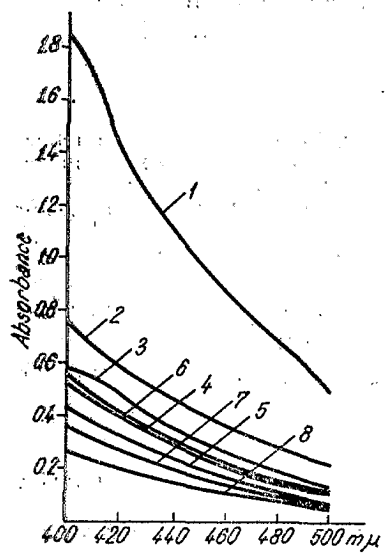

Fig. 7 — Results of dsicolouring of a dark-coloured oil:

1 — raw oil; *2*—neutralized oil; *3* — bleached oil 0.5% bleaching earth; *4*—bleached oil 1.0% bleaching earth; *5*—bleached oil 2.0% bleaching earth; *6* — bleached oil 1.0% bleaching earth + Decolor A; *7* — bleached oil 2.0% bleaching earth + Decolor A; *8* — bleached oil 3.0% bleaching earth + Decolor A(all oils in 15% hexane solution).

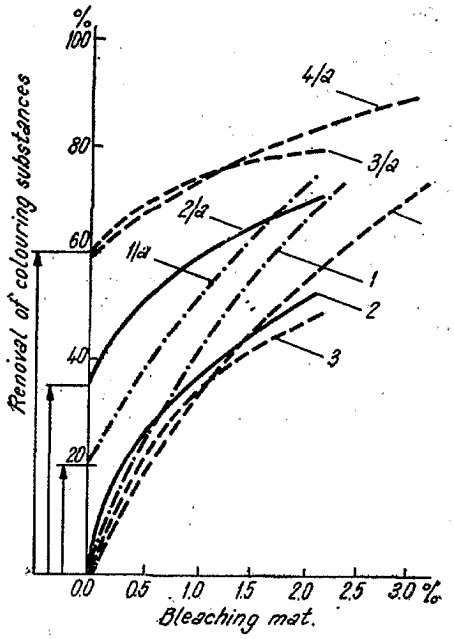

Fig. 8 — Summarized effect of discolouring procedures:

Removal of colouring substances of light colour oil: *1*—Calculated on neutralized oil (bleaching earth); *1-a*—Calculated on raw oil. *Removal of colouring substances of brownish oil*: *2* — Calculated on neutralized oil (bleaching earth); *2/a*—Calculated on raw oil. *Removal of colouring substances of dark colour oil*: *3* — Calculated on neutralized oil (bleaching earth); *3/a* — Calculated on raw oil; *4* — Calculated on neutralized oil (bleaching earth + Decolor A); *4/a* — Calculated on raw oil (bleaching earth + Decolor A);

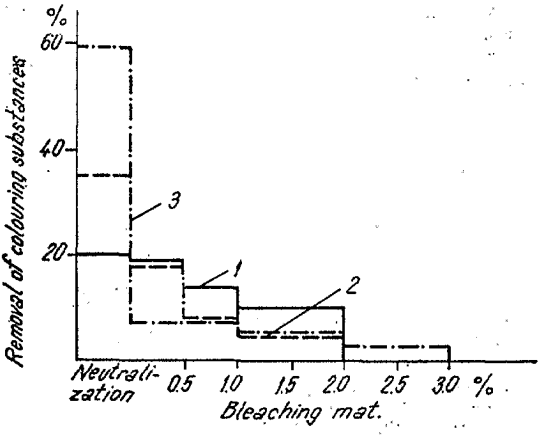

Fig. 9 — Effect of one individual discolouring procedure:

1 — light-coloured oil (bleaching earth); *2*—brownish oil (bleaching earth); *3*—dark-coloured oil (bleaching earth + Decolor A).

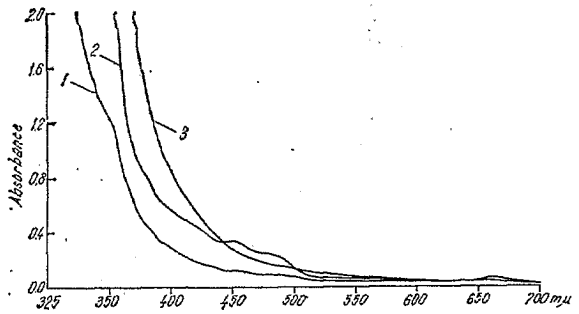

Fig. 10 — Absorption of a refined oil from dark-coloured oil in the visible region:
1 — 2 normal bleached oil; 3 — refined oil from dark-coloured oil.

— the activated bleaching earth has a relatively lower effect on the dark-coloured than on the light-coloreud sunflower oils ;

— this lower effect practically can be mended by the addition of the active carbon (20 per cent).

Table 5

Analysis data of disacidified and bleached refined product made of dark-coloured oil

Analysis	Limit-values specified in the standard (2)	
Taste, smell	tartish, sunflower, strange	strange smell nonpermitted
Iodine colour number	12	20
Density at 20°/20°C	0.920	0.915—0.927
Refraction index, at 20°C	1.4730	1.473—1.477
Acid number	0.20	2.0
Saponification number, %	190.3	186—196
Iodine number	129.7	110—143
Unsaponifiable matter, %	0.54	1.2 max.
Peroxide number	4.8	—
Impurities, %	0.05	0.5 max.
Vitamin E content, γ/g	165	—
Rapid rancidifying value, hours	5.1/2	—

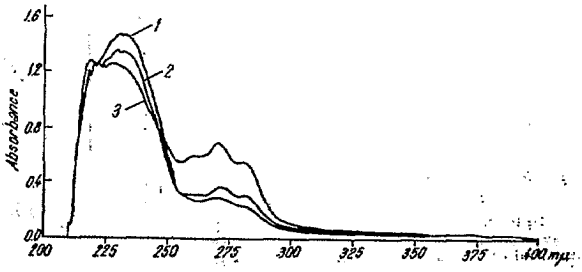

Fig. 11 — Absorption of a refined oil from dark-coloured oil in the ultra-violet region:
1—2—Normal bleached oil; *3*—refined oil from dark-coloured oil (all oils in 0.25% cyclo-hexane solution).

Data of investigation and analysis of the neutralized and bleached oil (3 percent Tonzil Decolor A mixture of 0.8 : 0.2 proportion) are given in table 5 and figures 10 and 11.

According to the data obtained the non-deodorized, refined oil meets the requirements of standard specification except for taste and smell characteristics. However, the vitamin E content is very low and the Swift values refer to a lower stability.

Based on previous experiences (10) we added therefore to the oil after bleaching 0.01 per cent of citric acid and 0.01 per cent of BHT-antioxidant. Thus the Swift value increased up to 7 hours.

The oil treated in this way could be stored for 5 months outside but at dark places covered with CO_2 gas without increasing the peroxide value over 8.

On the basis of the absorption in visible regions (figure 10) the colour of the oil is comparable to the colour of neutralized and bleached (0.5 per cent bleaching earth) oils obtained from light coloured standard raw oils.

However the ultra-violet absorption is characteristically high particularly in the triene region (figure 11).

In view of the refining losses both the brownish and the dark-coloured oil may be neutralized with a refining factor of about 2; bleaching losses change from 0.3 to 1.0 per cent with 1 to 3 per cent bleaching earth.

Thus the brownish dark-coloured sunflower oil can be refined with a loss of about 9 per cent, whereas the dark coloured oil with a loss of about 13 percent — including also the removed amount of fatty acids.

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