

## Physico Chemical Properties of higher polymers in petroleum Industry

\*Sudhaker Dubey \*\* Kartikeya Dwivedi \*\*\* Aarti Chaturvedi

\*\*\*\*Prashant Dwivedi

\* Maharaj Singh College ; C.C.S University;Meerut (U.P);India

\*\* Maharaj Singh College ; C.C.S University;Meerut (U.P);India

\*\*\*Maharaja Agrasen University;Baddi;Solen;(H.P) ;India

\*\*\*\* International College of Engineering;Uttar Pradesh Technical University ;Lucknow; (U.P) ; India

**Abstract:** - This paper deals with the phase inversion and the stability of emulsion. This phenomenon of inversion of emulsion is the sudden reversal of phase by which an oil/water emulsions becomes a water/oil emulsion. As the percentage of kerosene and turpentine oil increases from 10% to 90% in the oil/water emulsion, the oil/water type emulsion changes into water/oil types. There is a sudden fall in the conductance when oil phase concentration changes from 70-80% in all cases. The plots of log conductance against oil percentage shows that in all the cases horizontal portions are obtained. Thus for all the surfactants phase inversion from oil/water to water/oil occurs at an oil concentration of 70% in the case of both kerosene oil and turpentine oil. The lowest horizontal portion is indicative of water/oil emulsions. The highest horizontal portion corresponding to oil/water emulsions is case of RL-1, RL-2 & RL-3 up to a concentration of 30% oil, it is mainly oil/water emulsions. The study of stability shows that kerosene oil/water emulsion stabilized by adding 1% surfactant viz RL-1, RL-2,RL-3 remain stable upto 9 days, 9days and 19 days respectively. A demulsifier used in the petroleum industry to demulsify and the emulsion was tested here and found that emulsion stabilized by adding 1% RL-1 and RL-2 surfactant were stable upto 4 hours while emulsion stabilized by RL-3 surfactant remain stable upto 5 hrs respectively. After 10 hrs 100% demulsification is noticed in the case of all the emulsion.

**Keywords:** - emulsion, phase inversion, conductance, demulsification, surfactants.

### I. INTRODUCTION

The phenomena of phase inversion in emulsion i.e. the sudden reversal of phase by which an oil/water emulsion becomes water/oil emulsion (and vice-versa) is of considerable interest both from the practical as well as the theoretical point of view the importance resides in the fact that many commercial emulsion are prepared by, initially producing the wrong type of emulsions and inducing inversion to the desired type by addition of the phase which will ultimately be the external phase.

Robertson (1) was one of the first to record experiments of this kind, but his work was really an investigation on phase/volume relationship. Newmen (2) investigated two types of emulsions obtained with water and benzene. He found that when sodium-oleate was used as emulsifier, water was always the external phase. However, when magnesium-oleate was the emulsifying agent, he obtained emulsion of water/benzene type Newman found that emulsions of water/benzene stabilized by magnesium-oleate could be inverted by adding sufficient sodium oleate a phase inversion can some times be brought about on shaking an aged emulsion or both types can be prepared by the use of different types of mechanical methods.

The effect of electrolytes on emulsion is of great importance specially the divalent cations, normally found in hard water which tend to invert oil/water emulsion made with soaps and many other agents. Thus to an oil in water emulsion stabilized by sodium oleate and aluminium salts are added in a slight excess, the phase inversion takes place and water/oil emulsion is obtained.

Physical theories of emulsion inversion has been proposed which describe the formation of one type or the other to excess of positive or negative ions absorbed by the stabilizing film of the emulsifying agents. According to Clows (3) emulsion equilibrium depend on the relative proportion of the positive and negative ions absorbed by the film when negative ions are in excess the oil in water emulsion is favoured. Whereas an excess of positive ions has the reverse effect. The idea was accepted and extended by Bhatnagar(4) to explain the result of his own extensive experiments on the inversion of emulsion by electrolytes. Employing the electrical method suggested by Cayton(5) a sensitive means of detecting the inversion point. He found that(a) There is distinct valency effect of electrolytes. Trivalent electrolytes such as sulphates of  $Al^{+3}$  and  $Cr^{+3}$  are required in such a small amounts to effect inversion of oil/water emulsions than the bivalent electrolytes (b) The inverting capacity of the electrolytes follows the order  $Al>Cr>Ni>Pb>Ba>Sr$  and (c) The nature of the soap present influences the amount of electrolytes required to effect the reversal of phase. But the valency effect of the electrolyte still appears. He formulated two empirical rules from his results. (1) An emulsion of water/oil type can be transformed into one of the oil/water type by electrolytes having reactive ions like  $OH^-$  and  $PO_4^{3-}$ .

(2) An emulsion of oil/water type can be transformed into the reverse type i.e. water/oil type with electrolyte having reactive cations like  $Al^{3+}$  and  $Fe^{3+}$  and  $Th^{3+}$  Ostwald(6) & (7) apparently the first to point out the possibility of the existence of two emulsion types. Ostwald's theory is based on solid geometry, namely that in the assembly of spheres occupy 74.02% of the available space. Thus Ostwald was led to conclusion that if an emulsion contained more than 74% of the internal phase, inversion must necessarily occur, resulting in an emulsion of the opposite type which would contain only 26% internal phase. In other words in the regions 0-26% and 74-100% only one type of emulsion may exist in the intermediate region, both types are possible.

Bechere(8) shows the dependence of the inversion phase concentration on the emulsifier concentration for the inversion oil/water to water/oil. As the concentration of emulsifier increases the volume of the inversion phase at which the inversion occur decreases. The inversion concentration of an emulsion is a function of the concentration and the chemical nature of the surfactant. A Salager proposed that atleast two types of inversion occurs. A Catastrophic 'C' (9,10) inversion occurs when the inversion takes place because of the change in volume fraction (i.e. increasing the volume fraction of the dispersed phase it was first suggested that this inversion is caused by the complete coalescence of the dispersed phase at the closer packing arrangement of the drop(11).

Recently experiments were performed(12) for the surfactant/ oil-water system  $C_6H_{13}(OC_2H_4)OH/n$  tetradecane/aqueous 10 mL of NaCl at temperature from 298K down to 285K near the lower critical end point temperature.

Morphologies and phase volume fraction at which inversion occurred were determined for emulsion by electrical conductivity measurements. The inversion-hysteresis lines were found to confirm the dispersion-morphology diagram proposed by Smith(13).In the literature cited above following techniques have been utilized in the detection of phase inversion.

- 1) The Indicator Method:- In this method a oil soluble water insoluble or water soluble dye is dusted on the surface of emulsion to be examined. If the oil phase is continuous, the oil soluble dye will gradually spread throughout the system owing to its dissolving in the oil. If however, water is continuous phase, then dye will not spread.
- 2) The Drop Dilution Method:- The principle of this method is that emulsion can be diluted by addition of the external or continuous phase by not by adding the disperse phase.
- 3) The Electrical Conductance Method:- Bhatnagar(14) proposed a way of differentiating between oil/water and water/oil emulsion . A water continuous phase would be expected to show a very much higher conductance than an oil continuous phase sudden rise or fall in the conductance could be imply phase inversion during investigation.

In the present investigation phase inversion studies of oil/water emulsion stabilized by surfactants (RL-1,RL-2 and RL-3) has been carried out by measuring the electrical-conductance of the emulsion.

## II. EXPERIMENTAL

Materials:- Double distilled kerosene and turpentine oil having specific gravity 0.7948 g/mL and 0.9145 g/mL at 70°C respectively were stored to use in all the experiments. Double distilled water (conductance  $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) was employed throughout the course of investigations.

RL-1, RL-2 & RL-3 surfactants studied were synthesized as described Daitrolite 400 demulsifier was obtained from Daichi-chemical Bombay.

### Preparation of Emulsion:-

- (a) Oil/water emulsion of kerosene and turpentine oil were prepared by taking concentration of each of the single surfactant viz, RL-1, RL-2 and RL-3. The percentage of oil phase was then varied as 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% respectively

- (b) For demulsification studies, oil/water emulsion of kerosene were, prepared by taking concentration each of the single surfactant viz RL-1, RL-2, and RL-3. Oil/water was kept 1:1 constant. Demulsification was studied with the treatment of 50ppm Daitrolite, 400 and without demulsifier. The emulsion were prepared by agent in water method(15) by adding oil with constant stirring to the aqueous solution of surfactant and then finally agitated by redimix mixer to prepare final emulsion.

Measurement of Conductance:-

Conductance of emulsion was measured by German make (WTW) conductance meter with magic eye(16). The conductance of kerosene oil/water and turpentine oil/water emulsion having surfactant concentration 1% and obtaining varying percentage of oil in the range of 10% to 90% at room temperature viz  $25\pm 1^{\circ}\text{C}$  respectively have been measured and the result are summarized in table 1-II and figure 1-6.

- (c) Measurement of Demulsification :- The demulsification was measured by keeping emulsion samples in the carked measuring cylinders in the oven at  $25\pm 1^{\circ}\text{C}$ . The demulsification phenomena was observed visually with time. After creaming when the breaking of emulsion started, the separated oil also measured regularly at the interval 0-1,10, 20,30,40, 50 and 60 days while by adding demulsifier emulsion sample were checked at the interval of 0-4,5,6,7,8,9, and 10 hours respectively. Results presented in the table III and IV.

### III. RESULTS & DISCUSSION

The table I & II and figure 1-6 reveals that when in the experiments kerosene and turpentine oil were added to the 1% (aqueous solution of surfactant) and agitated for final emulsification in mixer, oil/water emulsion were initially formed. When the percentage of oil phase, were increased by adding different amounts such as 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% respectively, the oil/water emulsion change to water/oil type.

While studying the effect of phase volume ratio, it is evident from the table that there is sudden fall in conductance when oil phase concentration changes from 70% to 80%. Both in all the cases, the better picture emerges when log conductance is plotted against the oil phase concentration represented in figure 1-6. In all the cases three horizontal portion are obtained. Thus for all the surfactants, phase inversion from oil/water to water/oil occurs at an oil concentration of 70% in the case of both oil. The lowest horizontal portion is indicative of water/oil emulsion. The highest horizontal portion corresponds to oil/water emulsions. While the middle horizontal portion shows the mixed-emulsion profile. The phenomena of phase inversion is of significance both from practical as well as the theoretical point of view, many times a commercial emulsion initially of the wrong type may be obtained and later on change to the desired type by addition of suitable phase. Various theories have been advanced in order to explain the phenomena of phase inversion. According to Clows(17) the droplets of the internal themselves into filaments which weave around the experiments phase. The result is that the external phase breaks down into internal phase while the filaments coalesce in the process changing into continuous or external phase. According to Schulman & Cockbain (8) the process of phase inversion is supposed to consist loose flocculation of droplets of internal phase, whereby the external phase is trapped in the interior of the flocculate. The internal phase where (say the oil) coagulate due to reorganization of the emulsifying agent at the oil/water interface while external phase (say water) is dispersed in the form of irregularly shaped sacks and the oil/water emulsion change into water/oil type. Ostwald (10,11) has, proposed a simple stereometric theory based on the fact of solid geometry viz. in assembly of uniform share, arranged in closest possible packing, the space occupied by them would be 100% of the total. Accordingly, if an emulsion contained 74% of internal phase, inversion should occur producing the opposite type emulsion containing only 26% of internal phase. In the other words in the region 0-26% and 74-100 only one type of emulsion exist while in intermediate range both types are possible. In the present investigations the horizontal portions observed from 0-30% & 70-100% shows one type of emulsion and middle horizontal portion shows the mixed emulsion are in general agreement with Ostwald's theory.

Thus in the range 70-100% of oil, it is purely water-oil emulsion, while in the range of 0-30%, it is purely oil/water system. In the intermediate range both the systems occurs as would be obvious from the figures. Table -III and IV shows that the demulsification data of oil/water emulsions of kerosene oil, stabilized by adding surfactants viz RL-1, RL-2, RL-3 respectively. The results shows that emulsion stabilized by RL-1 and RL-2 were stable upto 9 days, after the preparation of emulsion and then at 10<sup>th</sup> day clearing start in the case of both the emulsions. In case of emulsion stabilized by RL-3 surfactant, breaking of emulsion starts on 20<sup>th</sup> day and oil separation on 50<sup>th</sup> day onward respectively, on 60<sup>th</sup> day complete breaking of emulsion is noticed. While emulsion stabilized by RL-2 shows creaming on 10<sup>th</sup> day, after preparation of emulsion on 40<sup>th</sup> day and complete breaking on 60<sup>th</sup> day respectively. The emulsion stabilized by surfactant RL-3 shows emulsion remain stable upto 19<sup>th</sup> day and after that creaming start and emulsion breaking starts an 40<sup>th</sup> day and breaks completely after 60<sup>th</sup> day.

A demulsifier used in petroleum industry to demulsify emulsion is checked for efficiency. The results shows, that emulsion stabilized by RL-1 and RL-2 remain stable upto 4 hours while emulsion stabilized by RL-3

surfactant remain stable up to 5 hours respectively. After 9<sup>th</sup> hour 80%, 75% and 70% oil get separated in cases of emulsion stabilized by RL-1, RL-2 and RL-3 surfactant respectively. After 10 hours 100% demulsification is achieved in all the cases.

Emulsification studies carried out in the earlier papers and in this paper reveal that physio-chemical properties such as surface tension, viscosity, particle size and conductance are the parameters which provides information regarding the formation of emulsions and maintaining their stability. Our result shows that lower the surface tension and higher the values of viscosity, particle size, and conductance favors emulsification and makes the emulsion more stable.

**Table-I**

Sl. No.	Oil Phase	Conductance RL-1	Ohm RL-2	cm RL-3	Type of Emulsion
1	10	-5.775	-5.762	-5.755	O/W
2	20	-5.807	-5.833	-5.856	O/W
3	30	-5.867	-5.875	-5.890	O/W
4	40	-6.097	-6.036	-6.070	O/W/ O/W
5	50	-6.195	-6.036	-6.100	O/W+ O/W
6	60	-6.208	-6.100	-6.126	O/W+ O/W
7	70	-6.266	-6.180	-6.204	O/W+ O/W
8	80	-7.833	-7.848	-7.863	O/W
9	90	-7.862	-7.877	-7.890	O/W

**Table-II**

Sl. No.	Oil Phase	Conductance RL-1	Ohm RL-2	cm RL-3	Type of Emulsion
1	10	-5.750	-5.780	-5.828	O/W
2	20	-5.903	-5.920	-5.955	O/W
3	30	-6.012	-6.063	-6.088	O/W
4	40	-6.092	-6.100	-6.173	O/W/ O/W
5	50	-6.106	-6.110	-6.173	O/W+ O/W
6	60	-6.115	-6.160	-6.181	O/W+ O/W
7	70	-6.124	-6.210	-6.241	O/W+ O/W
8	80	-7.121	-7.041	-7.052	O/W
9	90	-7.152	-7.062	-7.074	O/W

**Table-III**

Sl.	Time	RL-1	RL-2	RL-3
1	01	stable	stable	stable
2	10	creaming	creaming	stable
3	20	creaming	creaming	creaming
4	30	breaking	creaming	creaming
5	40	breaking	breaking	breaking
6	50	60% oil separated	breaking	breaking
7	60	70% oil separated	50% oil separated	40% oil separated

Table-IV

Sl. No.	Time in Days	RL-1	RL-2	RL-3
1	0-4	stable	stable	stable
2	5	creaming	creaming	stable
3	6	breaking	creaming	creaming
4	7	breaking	breaking	breaking
5	8	60% oil separation	breaking	breaking
6	9	80% oil separation	75% oil separation	70% oil separation
7	10	100% oil separation	100% oil separation	100% oil separation

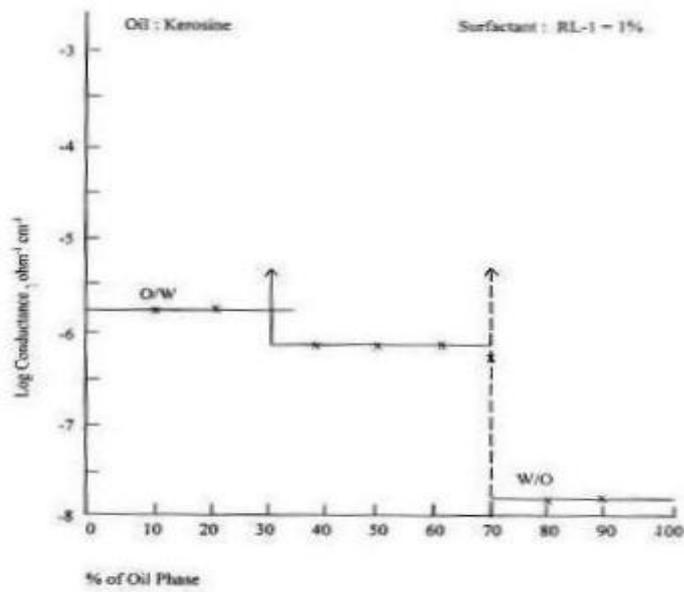


Fig-1: Phase Inversion of Emulsion

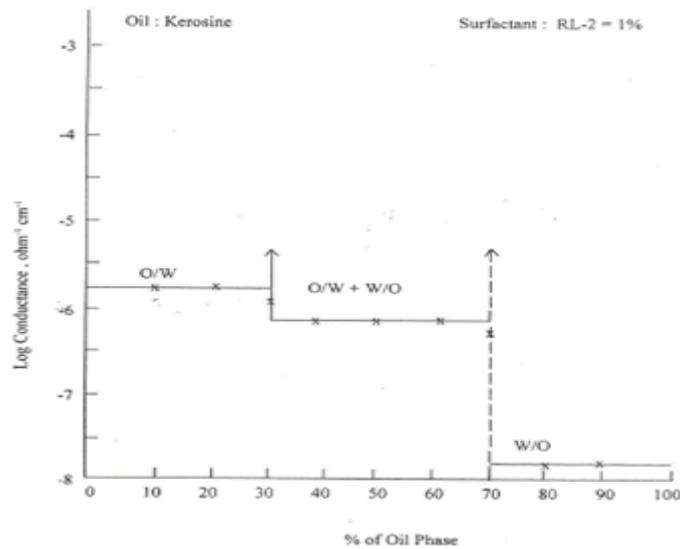


Fig-2: Phase Inversion of Emulsion

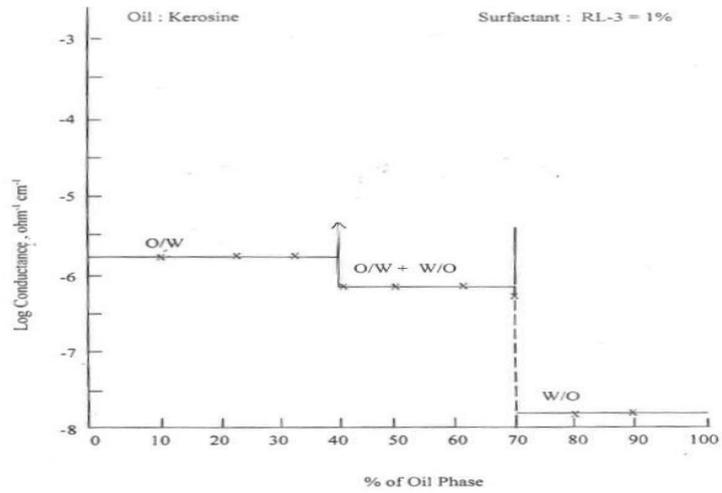


Fig-3: Phase Inversion of Emulsion.

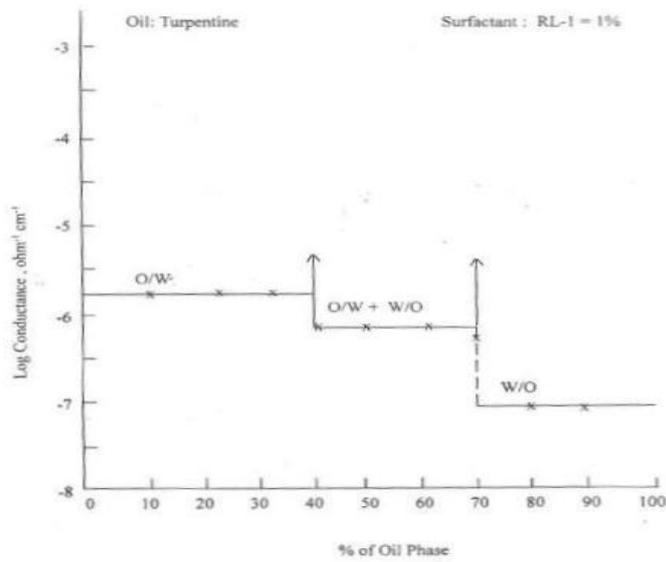


Fig-4: Phase Inversion of Emulsion

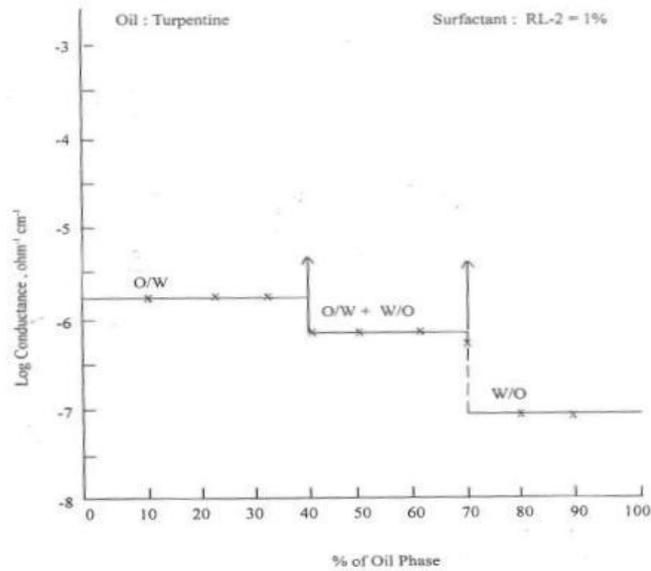
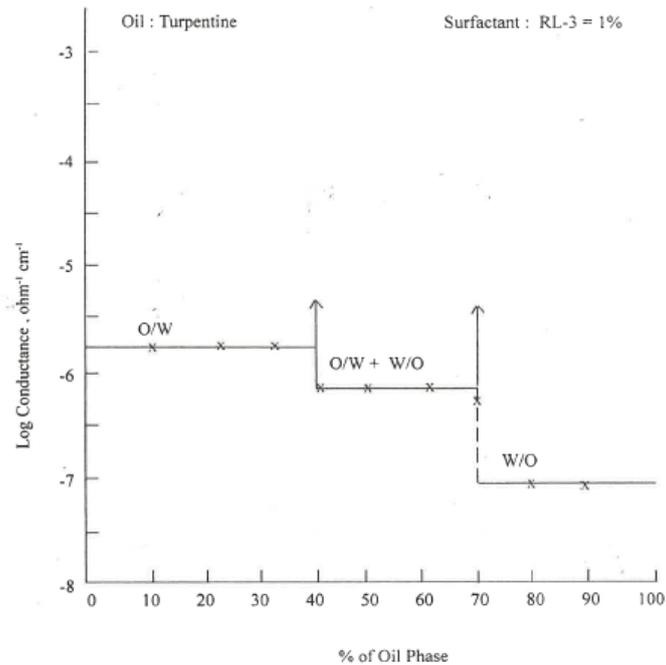


Fig-5: Phase Inversion of Emulsion



**Fig-6:- Phase Inversion of Emulsion**

#### REFERENCES

- [1] Robertson K. Kolloid-z, 77, 1910.
- [2] Newman J., Phys. chem 18-34, 1914.
- [3] Clows G.H.A., Proc. Soc. Exp. Biol And-med 11, 1, 1913.
- [4] Bhatnagar, S.S. J. chem soc. 119, 61, 1921.
- [5] Clayton W., Britcoll. reports 2, 114, 1918.
- [6] Ostwald W.O., Kolloid-Z, 6, 103, 1910.
- [7] Becher, P., J. Soc. cosmetic chem., IX, 3, 141, 1958.
- [8] Salager J.L., Phase transformation and emulsion inversion on the basis of catastrophe theory in P. Becher (Ed) Encyclopedia of emulsion science, vol 3, Marcel-Dekker New York 99, 79-134, 1988.
- [9] B.W. Brooks, H.N. Reymond, phase inversion non ionic surfactant-oil-water-system-3. The effect of oil phase viscosity on catastrophic inversion and the relationship between the drop sizes present before and after catastrophic inversion; chem.-eng. sic. 49, 1843-1853, 1994.
- [10] Ostwald w., Emulsion Kolloids Z., 8, 103-109, 1910, chem. Abs. 1705.